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CATALYTIC HYDROGENATION AND REDUCTION

E. B. MAXTED

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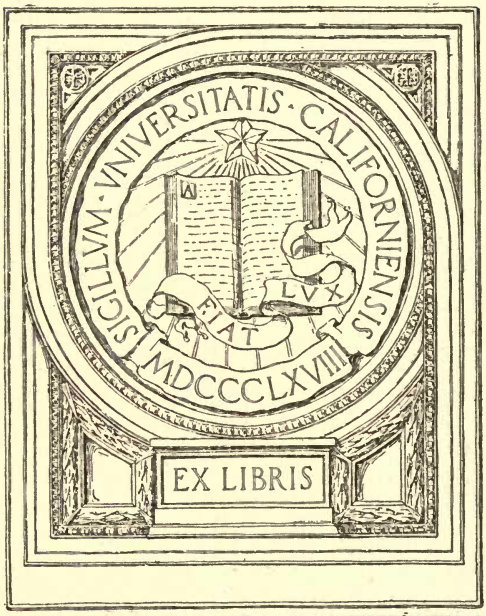
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CATALYTIC HYDROGENATION AND REDUCTION

BY

EDWARD B. MAXTED, PH.D., B.SC., F.C.S.

With 12 Illustrations

UNIV. OF CALIFORNIA

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PREFACE

THE present volume has been written with the object of presenting in an easily accessible form the numerous examples of catalytic hydrogenation which have from time to time been published.

Special attention has been given to experimental methods and, in addition to the simple hydrogenation of unsaturated linkages, such as the conversion of ethylene to ethane or of benzene to cyclohexane, various catalytic reductions of a less simple nature, usually involving the splitting off of water or of a halogen acid, have been included. A chapter has also been devoted to dehydrogenation.

E. B. M.

WALSALL.

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CATALYTIC HYDROGENATION

CHAPTER I

WHILE it has long been known that hydrogen *in statu nascendi* possesses a very much more active character than the comparatively inert free gas, any systematic investigation of the results obtainable by activating free hydrogen by the presence of catalysts belongs almost entirely to the last two decades. The subject received its impetus by the discovery of the hydrogen-activating properties of nickel by Sabatier and Senderens in 1899, and by the commercial application of the reaction to the hydrogenation of unsaturated glycerides. True it is that M. P. de Wilde in 1874[1] found that acetylene is hydrogenated to ethane in presence of platinum black, that M. Saytzeff and Kolbe[2] as long ago as 1871 had succeeded in reducing benzoyl chloride, nitrobenzene, and nitromethane by leading the vapours of these bodies, mixed with hydrogen, over palladium black, and that Cooke[3] in 1888 had carried out various reductions in presence of platinum but, save for these isolated results, catalytic hydrogenation had received little attention up to the time of Sabatier's work.

Free hydrogen in presence of a catalyst is often

[1] M. P. de Wilde, *Ber.* 1874, **7**, 353.
[2] Saytzeff and Kolbe, *J. prakt. Chem.* (N.F.), 1871, **4**, 418; 1872, **6**, 128.
[3] Cooke, *Chem. News*, 1888, **58**, 103.

more active than that in a nascent condition ; thus while oleic acid is scarcely affected by nascent hydrogen, it is easily and quantitatively reduced to stearic acid by free hydrogen in the presence of a catalyst.

Catalytic hydrogenation has rendered easy the preparation of many aromatic derivatives and even of bodies of an extremely complicated nature, such as reduced alkaloids. The introduction of saturating hydrogen is by no means limited to the saturation of ethylenic, benzenoid, or triple bonds between carbon atoms, but finds application also *inter alia* in the hydrogenation of linkages between carbon and nitrogen, carbon and oxygen, nitrogen and nitrogen, and nitrogen and oxygen.

It is, further, possible to effect catalytically many reduction reactions which do not consist merely in the introduction of hydrogen, such as the reduction of the carbonyl group CO to CH_2, of the group CH·OH to CH_3, and of metallic oxides to metal.

The metallic catalysts, on the surface of which the hydrogen exists in an active condition, may conveniently be divided into two classes. To the first class belong the metals of the iron group—iron nickel, and cobalt, together with copper. These, metals begin, in general, to exert a marked activating influence on hydrogen only at an elevated temperature. The minimum temperature at which activity begins to be developed is different for each metal, and there exists, in general, a definite optimum temperature for each catalyst, in the determination of which the reaction to be carried out also plays an important part, and above which temperature the activity of the catalyst, instead of becoming increased by increasing temperature, begins to decrease. Thus, while metallic nickel begins to effect the addition of hydrogen to the ethylenic linkage in an unsaturated glyceride at temperatures not far above 100° C., activation to a satis-

factory degree does not take place till nearer 150° C., and the optimum temperature, at any rate as far as velocity is concerned, is considerably higher than this.

The minimum temperature at which the metals of the first class begin to exert activity is, in general, higher for cobalt than for nickel, for copper than for cobalt, and for iron than for copper. Thus, from this point of view, the series may be written: nickel, cobalt, copper, iron, in ascending order of minimum activating temperature. The order of activity of these metals at any given temperature, at any rate for moderate temperatures, varies from metal to metal in the same direction, nickel being more active than cobalt, cobalt than copper, and copper than iron.

In determining temperatures, it is to be noted that we are only able to ascertain the mean temperature of the space surrounding the seat of reaction. It is probably fair to assume that the actual seat of reaction is in a very different thermal condition from the main bulk of the substance which is being hydrogenated.

It is, further, interesting to note that silver, which is so nearly related chemically to copper, has been found by Paal and Gerum to be slightly active for the reduction of nitrobenzene to aniline at 80° C. The use of finely divided silver and gold at 200–250° C. for the catalytic reduction of nitrobenzene to aniline has been protected by the Badische Anilin- & Soda-Fabrik.[1]

To the second class of catalysts belong the metals of the platinum and palladium groups, consisting of ruthenium, rhodium, palladium, osmium, iridium, and platinum. Of these, platinum and palladium have been more extensively used than the other metals of the family. All members of this group of metals are active at the ordinary temperature,

[1] Badische Anilin- & Soda-Fabrik, German patent, 263396.

osmium being by far the least active. Directions for the preparation of the various metals for catalytic purposes will be found in the second chapter of this book.

It is to be noted that, instead of introducing the metals in the metallic form into the substance to be hydrogenated, an oxide or salt of the metal may often conveniently, and sometimes even advantageously, be substituted, provided that under the conditions of the reaction a sufficient amount of reduction of the oxide or salt by the hydrogen takes place. Thus instead of platinum black, platinum chloride may be introduced, or instead of metallic nickel, nickel oxide or a suitable salt such as the formate.

For the success of the reaction, it is in general necessary that catalyst poisons such as sulphur compounds, arsenic and phosphorus and their compounds, carbon monoxide and lead and its compounds should be absent. In certain cases, however, such as in the hydrogenation of unsaturated glycerides by nickel, the catalyst itself may contain a considerable amount of sulphur as sulphate or even as sulphide without any very bad effect being observed, while in other reactions, such as the hydrogenation of benzene to cyclohexane, the smallest trace of sulphur in the form of thiophene is sufficient to stop the reaction.

Besides chemical poisoning from impurities, in the substance to be hydrogenated, in the catalyst, or in the hydrogen, a second form of poisoning of a more mechanical nature is sometimes found in reactions in liquid media, where colloidal or other impurities may settle on the surface of the catalyst and thus clog its action. This clogging of the catalytically active surface is also observed in gas reactions.

We have at present very little experimental evidence as to the part played by the catalyst in

the activation process or as to the actual course of the reaction itself. Sabatier supposes that the reaction depends on the intermediate formation of an unstable metallic hydride, but a good case can also be made out for action of a more physical nature. A theory as to the activity of the metallic oxides themselves, as well as the metals, has lately been advanced, but it should be emphasised that, while there are many examples of activity in catalysts consisting of oxide-free metals, no activity of oxides has been observed under conditions where reduction of the oxide by hydrogen to a considerable extent has not already taken place or is not possible.

CHAPTER II

The Preparation of Catalysts

A. The Nickel Group (Ni, Fe, Co, and Cu)

This group contains the catalysts originally used by Sabatier and Senderens. For the preparation of these metals in an active form, attention must be paid, not only to the purity of all materials used, but also to the highest temperature to which the metallic oxide or salt is subjected both immediately before the production of the actual catalyst and during the course of the catalytic reaction itself. The purity of the materials is rather to be reckoned from the point of view of the absence of catalyst poisons than from the ordinary chemical viewpoint of purity. Thus while the presence of extremely small quantities of arsenic or its compounds interferes seriously with the activity of the catalyst, the presence of a non-poisonous foreign substance may not only have no harmful effect but may even exert a beneficial influence on the activity. The subject of promoters—the opposite of catalyst poisons—becomes an important one where, for commercial or other reasons, it is desired to carry out the reaction as rapidly as possible.

For the production of a nickel catalyst, a nickel salt which has been manufactured from nickel produced by the Mond carbonyl process should be employed. In many cases it is almost immaterial

which salt of this pure nickel is taken, even the sulphate, although it contains a catalyst poison, giving almost as good a catalyst, for instance for the hardening of oils, as the poison-free, but more expensive, nitrate.

The exact method of preparing the catalyst depends largely on how it is to be employed when made. Thus for the hydrogenation of benzene or oleic acid by the vapour method, it is preferable to support the nickel in such a way that it presents a large active surface without stopping the passage of gas through the reaction chamber. For purposes of this sort asbestos rope or pumice may be thoroughly cleaned by treatment with dilute nitric acid, followed by ignition. The asbestos or pumice is soaked in nickel nitrate melted in its water of crystallisation, or in a strong solution of the salt, and heated to the lowest temperature necessary for the conversion of the nitrate to oxide. The oxide, thus supported, is introduced into the actual tube or vessel in which hydrogenation is to be carried out and reduced there by means of pure hydrogen, preferably immediately before it is required.

The nature of the catalyst will vary largely with the temperature at which it is reduced. In general, after a certain minimum has been passed, the lower the temperature of reduction the higher will be the activity, though the keeping down of the reduction temperature below that at which it is proposed to carry out the catalytic reaction means only that the time required for the catalyst preparation is lengthened without ultimate gain in activity.

Reduction at a comparatively high temperature, while detracting from the activity of the catalyst, is in general conducive to the development of a higher power of resistance to the action of catalyst poisons. Nickel oxide, if prepared without overheating, is reduced slowly by hydrogen at about 200° C., and Sabatier and Senderens recommend

that the reduction should be carried out at a temperature slightly below 300° C. From 300–350° C. is, however, perhaps the most suitable temperature for general work by the vapour method.

Instead of heating the supported nickel nitrate and transforming it thus to oxide, the nitrate may be treated with a solution of sodium or potassium hydroxide or carbonate, followed by a thorough washing with distilled water, while in place of employing asbestos or pumice coated with nickel as the catalyst, an excellent result may be obtained by employing porous briquettes containing nickel or nickel oxide.

The following example illustrates a method of making briquettes for purposes such as the reduction of benzene to hexahydrobenzene. Nickel nitrate is dissolved in distilled water and to the solution magnesium nitrate is added in sufficient quantity to give with soda a weight of magnesium oxide equal to the nickel in the nickel nitrate. The mixed nitrates are precipitated with sodium hydroxide or carbonate, and the precipitate, after being washed with distilled water, is spread with a nickel or porcelain spatula, as a layer of about a quarter of an inch thick, on a clean, square sheet of nickel. The moist mass is conveniently divided into squares of suitable size by means of a needle mounted in a wooden holder, when it may be dried by the cautious and gentle application of a Bunsen flame to the supporting nickel plate.

The above remarks apply more especially to hydrogenation by the vapour method. For the hydrogenation of liquid or dissolved substances it is usual to employ the nickel catalyst in the form of a suspension and to remove the nickel particles after the operation by filtering.

The nickel catalyst for suspension in the liquid may be prepared by reducing pure nickel oxide or carbonate by means of pure hydrogen at 300–320° C.,

or even at a slightly higher temperature. The oxide or carbonate should be precipitated from nickel sulphate, or preferably nitrate, by pure sodium carbonate or hydroxide, or it may be prepared by gently heating the nitrate to the lowest temperature required for its conversion to oxide.

For laboratory purposes, the reduction of the oxide to metal is conveniently carried out in a distilling flask heated on a sand-bath. The oxide should not fill more than a quarter of the flask at the most, and this must be frequently shaken in order to expose fresh surfaces of oxide or carbonate to the action of the hydrogen. From two to three hours' reduction at 320–350° C. should be amply sufficient to obtain an active catalyst when working with a 300 c.c. distilling flask one-quarter full of nickel oxide, provided that a fairly rapid current of hydrogen be used. With less oxide, reduction would probably have proceeded to a satisfactory degree in less time. It is to be noted that complete reduction to metal never takes place under ordinary conditions of working at these comparatively low temperatures, and, further, that unnecessarily prolonged reduction reduces the activity of the catalyst.

For certain reactions it is possible and sometimes preferable to effect the reduction in the liquid itself. This is particularly the case where non-volatile liquids boiling at above 280° C. are to be hydrogenated by the bubbling method, and where there is no danger of the body decomposing at the temperature employed. Reduction of the oxide or salt in liquid media may be carried out at considerably lower temperatures than 300° C.; for instance, Bedford and Williams recommend 255° C. as a suitable reduction temperature for nickel oxide in the presence of an unsaturated glyceride.

If the nickel oxide is reduced dry, it is preferable that this should be done immediately before use, the reduced nickel being allowed to cool completely

in the current of hydrogen before the liquid to be treated is run in. In order to increase the surface of the nickel, the oxide, from which the catalyst is prepared, may, if desired, be supported on an inert substance such as kieselguhr or carbon. To do this, the nitrate or sulphate solution, from which the oxide is made, is mixed with kieselguhr in the proportion of from two to ten parts of kieselguhr to one of metallic nickel and the precipitation of the oxide or carbonate carried out with constant stirring.

The other members of this group of catalysts are of far less importance than nickel from the point of view of the extent to which they are used. Copper is chiefly used for hydrogenation reactions in which a milder action is required than would be obtained with nickel. Sabatier and Senderens[1] recommend a reduction temperature for copper of slightly under 200° C. Iron and cobalt are even less used than copper. Iron is prepared by reduction of its oxide or carbonate at 400–500° C., cobalt at a slightly lower temperature than this. The remarks made under nickel with respect to the manufacture of the catalyst also apply to iron, cobalt, and copper. Cobalt is usually less active than nickel and more active than copper. Iron is only at its best slightly active and is for many reactions inactive, the initial temperature at which iron becomes active being far higher than for the other metals.

In certain cases, where the substance to be hydrogenated is extremely sensitive to the presence of small quantities of poisons, an impure catalyst may be rendered efficient by alternate reduction with pure hydrogen and oxidation with pure oxygen provided that the final reduction be carried out at a comparatively low temperature, or instead of being reduced directly the purified oxide may be dissolved in pure nitric acid and worked up as usual.

[1] Sabatier and Senderens, *Compt. rend.*, 1900, **130**, 1761; 1901, **133**, 321.

The above methods of preparation all treat of the reduction of an oxide at moderate temperatures by hydrogen. Certain inorganic or organic nickel or other metal salts, such as lactate, formate, or carbonate, may be substituted for the oxide with the production of catalysts possessing a high activity. The production of nickel by the decomposition of the carbonyl has also been proposed.

The Platinum Group.

While the metals of the nickel group are usually used for hydrogenation reactions at high temperatures between gases and for the industrial hydrogenation of such liquids as the natural fats and their acids, the catalysts of the platinum group have principally been employed for the hydrogenation of substances in the liquid or dissolved condition, at the ordinary temperature or at temperatures not very far removed from this. If the reaction is to be carried out in a liquid, the state of division of the catalyst is of the utmost importance as a factor for determining the velocity of the reaction, and for this reason the introduction of colloidal catalysts by Paal and others has rendered possible the carrying out of many hydrogenation reactions which would have been unattainable with less finely divided catalysts owing to the slowness with which they proceed and the ease with which they are stopped by poisons.

Salts of the platinum metals are very easily reduced to the metallic state by such reducing agents as free or nascent hydrogen in the cold, formaldehyde, hydrazine, etc., but in general the metal is produced in a flocculent condition possessing the disadvantage of a comparatively small catalytic surface.

A non-colloidal platinum catalyst may be pre-

pared according to Löw's[1] method by dissolving 5 grams of platinic chloride in 5–6 c.c. of water and mixing in 7 c.c. of a 40–50 per cent. solution of formaldehyde. Ten grams of a 50 per cent. sodium hydroxide solution are added and the mixture is allowed to stand for twelve hours. The platinum may be washed on a Buechner funnel until the wash-water runs through black, or the alkaline liquid may be warmed for a quarter of an hour to 50° C. and washed by decantation till the washings no longer give a reaction with silver nitrate.[2]

For some purposes, a sufficiently active catalyst is obtained by suspending or dissolving the platinum chloride in the substance to be reduced, or in any suitable solvent, and passing free hydrogen at about 100° C. or even less, sodium carbonate being added in quantity sufficient to neutralise the hydrochloric acid liberated. Thus with an unsaturated glyceride, such as refined olive oil, rapid hydrogenation is obtained by this simple method of treatment even when using only 0·1 per cent. of platinum, or an even smaller quantity of palladium.[3]

Colloidal metals of the platinum group were prepared in very dilute solution by Bredig[4] by his disintegration method; by Lottermoser,[5] by reduction of a solution of platinic chloride by means of formaldehyde in presence of alkali; by Gutbier,[6] by reduction with hydrazine hydrate; by Henrich,[7] using pyrocatechin, and by Garbowski[8] with tannin, gallic acid, and other organic reducing agents. These dilute solutions of the colloid metals are of little use for catalytic hydrogenation, by reason of

[1] Löw, *Ber.*, 1890, **23**, 289.
[2] Willstätter, *Ber.*, 1912, **45**, 1472.
[3] Paal, U.S. patent 1023753 (1912).
[4] Bredig, *Anorg. Fermente*, Leipzig, 1901.
[5] Lottermoser, *Über anorg. kolloide*, Stuttgart, 1901.
[6] Gutbier, *Zeit anorg. Chem.*, 1902, **32**, 352.
[7] Henrich, *Ber.*, 1903, **36**, 609.
[8] Garbowski, *ibid.*, 1903, **36**, 1215.

the ease with which they are coagulated by electrolytes.

The necessary stability is easily obtained by the use of a so-called protective colloid. C. Paal and C. Amberger[1] use for this purpose sodium protalbate or lysalbate, two products of the degradation of egg-albumin by means of aqueous alkalies, hydrazine being stated to form the most suitable reducing agent for the preparation of colloidal platinum or palladium. Hydroxylamine and formaldehyde were found to be unsuitable. For iridium, nascent hydrogen from sodium amalgam was used.

The following directions are given by Paal and Amberger[2] for the preparation of colloidal platinum. One gram of sodium lysalbate is dissolved in 30 c.c. of water, together with rather more sodium hydroxide than is necessary for reaction with the chlorine of the chloroplatinic acid taken. Two grams of chloroplatinic acid are now dissolved in a little water and added to the alkaline liquid, the clear dark brown solution being then reduced by means of a slight excess of hydrazine hydrate. The colloidal platinum thus produced is purified by dialysis, and may be obtained, by evaporating first on the water-bath and then to dryness in a vacuum, in the form of black plates, easily soluble in water to a black, opaque liquid. The product contains sodium lysalbate in addition to platinum. Colloidal palladium is obtained in a similar manner and sodium protalbate may be substituted for the lysalbate. In a later paper,[3] the above authors use gaseous hydrogen as the reducing agent.

Colloidal palladium prepared according to Paal and Amberger's method is not suitable for the hydrogenation of bodies in acid media, since in the presence of acids an adsorption compound of

[1] Paal and Amberger, *Ber.*, 1904, **35**, 124 *et seq.*
[2] Paal and Amberger, *ibid.*, 1902, **35**, 2195.
[3] Paal and Amberger, *ibid.*, 1905, **38**, 1398.

protalbic acid and palladium is precipitated. In order to avoid the coagulating of the catalyst, it is necessary to prepare the colloidal palladium in the presence of a protective colloid stable in the presence of acids. For this purpose, C. Kelber and R. Schwarz[1] recommend the colloid produced by the action of an organic acid on gluten. Colloidal palladium prepared according to the following directions is not coagulated by dilute mineral acids. Take 16 grams of a protective colloid solution, obtained by treating gluten with acetic acid and containing about 50 per cent. of the treated gluten. To this add 4 grams of palladium chloride dissolved in a little water. A little ammonia is added to the dark brown solution, followed by hydrazine hydrate, drop by drop. The liquid froths and gives off gas, becoming a deep brownish-black. As soon as the reduction is complete, the colloidal palladium preparation should be dialysed till the outside water gives no chloride reaction, after which it is cautiously evaporated down, finally in a vacuum. The product consists of black, lustrous scales, easily soluble in water and in glacial acetic acid.

In certain cases, direct reduction in presence of a protective colloid is sufficient for the preparation of a colloid catalyst, which may, where required, be purified by dialysing in the usual way. Thus Skita[2] finds that by reducing platinum chloride in presence of gum arabic and an unsaturated ketone a colloidal metal is produced. The colloid thus obtained may, where desired, be purified in the usual way by dialysis.

Perhaps the simplest method of preparing colloidal platinum or palladium catalysts, provided that a small sample of the colloidal metal is available, is by Skita's inoculation method. Equal parts of platinum or palladium chloride and gum arabic are

[1] Kelber and Schwarz, *Ber.* 1912, **45**, 1946.
[2] Skita, *ibid.*, 1909, **42**, 1027.

dissolved in a small quantity of water. A trace of colloidal platinum, prepared either as described by Skita and Meyer[1] or by any other suitable method, is added and the whole reduced by hydrogen, when the bulk of the reduced metal separates in a colloidal state. This is not the case if no colloidal metal is added. Colloidal solutions made as described are stable in the presence of glacial acetic acid and may be used for the hydrogenation of organic substances soluble in this but insoluble in water.

[1] Skita and Meyer, *Ber.*, 1912, **45**, 3579.

CHAPTER III

The Methods of Catalytic Hydrogenation

The methods employed for catalytic hydrogenation will be governed by the state of aggregation of the body to be treated, and by the temperature at which the proposed reduction can be most satisfactorily effected. The methods of treatment may therefore be divided into two classes, the first of which deals with the hydrogenation of gases, including the vapours of volatile substances, while the second relates to the hydrogenation of liquids.

Vapour Treatment.

The original hydrogenation work of Sabatier and Senderens was carried out by passing the vapour of various unsaturated organic bodies together with hydrogen over a catalytically active metal contained in a heated tube. A large excess of hydrogen is usually desirable, and complete saturation in one passage is seldom attained.

For cases where a very exact regulation of the relative proportions of hydrogen and unsaturated body is not necessary, the apparatus shown in Fig. 1 may be employed.

This consists of a distilling flask, *A*, containing the unsaturated substance and heated by a Bunsen flame, or, where the body is liable to boil with decomposition, by means of a water- or oil-bath. A current of pure hydrogen, obtained for convenience

from a cylinder, is passed into the distillation flask, and carries with it into the reaction tube, *B*, a

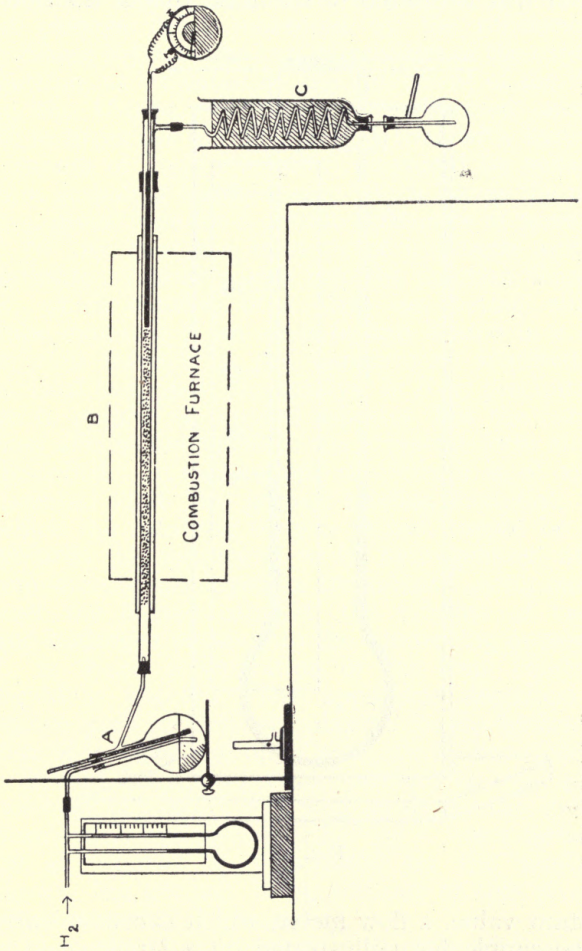


FIG. 1.

quantity of vapour depending on the temperature in *A*, and on the velocity of the current of hydrogen.

It is usually sufficient to regulate roughly this gas current by observing its rate of passage through *A*, but if it is desired to maintain this at a strictly

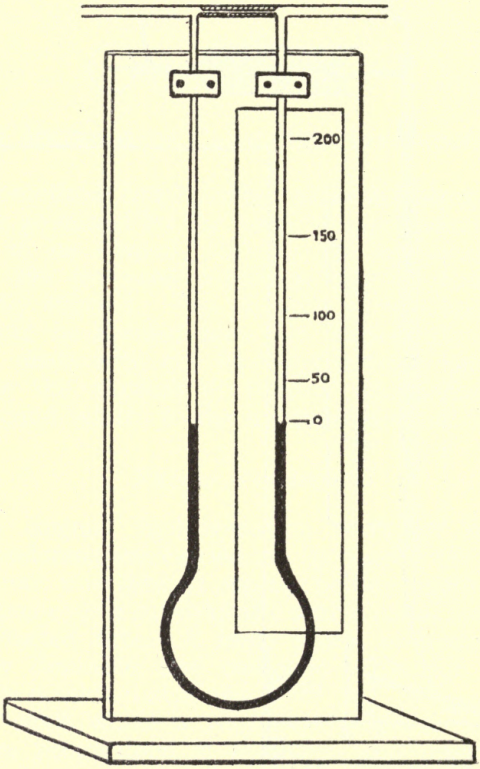


FIG. 2.

constant value, a flow meter, which is conveniently of the simple form illustrated on a larger scale in Fig. 2, may be interposed between the cylinder and the distilling flask.

This meter consists of a tube with a capillary constriction as shown in the figure, through which tube the hydrogen current is passed, the velocity of passage being measured by the difference in pressure between the two extremities of the capillary portion, as indicated by the movement of the liquid in the U-tube. The scale is calibrated once for all in litres per hour by actual trial with hydrogen currents of known velocity, measured by collecting in a gasholder the hydrogen which leaves the meter in a given time for a certain difference of pressure.

In any case the mixture of hydrogen and unsaturated vapour passes into the reaction chamber, *B*, which consists of a glass—or, better, silica—tube mounted in an air-bath and heated in a combustion furnace to the temperature required. It is usual to support the catalyst in *B* by precipitation on to pumice or purified asbestos, but the catalyst may also be employed in the briquette form already described. In making up briquettes it is, of course, essential that the porous binding material, with which the catalytic body is mixed, should be inert towards the compound to be hydrogenated at the temperature employed for treatment. After passage over the heated catalyst, the mixture of vapour and hydrogen passes into the condensing apparatus, *C*, in which a separation of gas from condensed liquid is effected. The apparatus described has shown itself particularly adapted for the hydrogenation of benzene and other aromatic hydrocarbons.

Should the hydrogenated product be solid at the ordinary temperature, a wide straight tube, inclined downwards and cooled either by a water-jacket or by air, should be substituted for the condenser shown, the product being run out of this receiver, when necessary, by warming.

If a more exact control of the rate of passage of the unsaturated body is desired, a bent burette may be substituted for the distilling flask as shown

in Fig. 7 (see Chapter V), which illustrates Sabatier and Senderens's original apparatus.

For the hydrogenation of permanent gases, such as ethylene and propylene, it is usually sufficient to mix these in a gasholder with the required volume of hydrogen and to pass the mixture over a heated tube containing catalyst, the product being collected in a second gasholder. In some cases, for instance with acetylene, the reaction is so vigorous that caution must be observed with regard to heating the catalyst employed, and the air-bath may be replaced by immersion of the reaction tube in a water- or oil-bath, the temperature of which is capable of being more accurately controlled, this bath being preferably provided with an automatic temperature regulator of any standard type.

Hydrogenation of Liquids.

The methods of procedure usually adopted on a laboratory scale for the hydrogenation of liquids may be subdivideed into three types, according to whether the necessary intimate contact between the liquid, gaseous and solid (*i.e.*, the catalyst) phases of the system undergoing treatment is induced by simple bubbling, by shaking, or by stirring respectively.

Hydrogenation by Bubbling.—The bubbling method, first described by Normann in 1903,[1] constitutes a simple and effective method of hydrogenating a non-volatile liquid. The liquid, containing a suitable catalyst in suspension, is contained in a conical beaker—or, better, in a distilling flask—a rapid stream of pure hydrogen, which serves the double purpose of agitation and hydrogenation proper, being led through. The distilling flask may be tilted in order to prevent expulsion of the liquid by the rapid current of gas, and the

[1] Normann, English patent 1515, 1903.

hydrogen inlet tube slightly bent, as in a distillation in steam. For a full discussion of the necessity for a rapid stream of hydrogen and of other necessary experimental conditions, more particularly from the point of view of the hydrogenation of oils by the bubbling method, the evidence given in the Patents case, Crosfield *v.* Techno-Chemical Laboratories, Ltd.,[1] may be consulted. The excess of hydrogen is usually large enough to preclude the determination of the degree of hydrogenation of the unsaturated body by a direct measurement of the hydrogen absorbed, but it is usually possible to estimate this indirectly, for instance by an iodine value determination.

A description of the standard methods employed for this is included in a later chapter.

Hydrogenation by Shaking, etc.—According to this method, with which are associated the names, *inter alia*, of Paal, Willstätter and Skita, the liquid to be treated is contained in a glass vessel of suitable size, mounted in a shaking apparatus and connected with a known volume of hydrogen, the absorption of which can be read off from time to time as the reaction proceeds. The method may be used for the reduction of liquids proper or of solids dissolved in a suitable solvent such as water, alcohol, glacial acetic acid, acetone, ether, or chloroform.

The apparatus employed will depend on the weight of substance taken, and on the temperature and pressure at which the reduction is to be carried out. In its simplest form and for work at atmospheric temperature and pressure it may consist of a shaking vessel, mounted in a shaker of any standard design, such as may readily be bought from stock or if desired constructed in the laboratory. This shaking vessel, *A*, is connected (see Fig. 3) to a gasholder of hydrogen, *B*, by means of a metal

[1] *Patents Journal*, **30**, Supplement, June 18, 1913, Reports of Cases No. 12.

spiral or thick-walled rubber tubing. If desired, access of moisture from the gasholder may be prevented in the usual way by the interposition of a drying tube containing freshly fused calcium chloride shown at *C*. For the preliminary displacement of air by hydrogen a side tap, *D*, is provided, connected when required to a vacuum, the hydrogenation vessel and drying tube being alternately evacuated (*E* being closed) and filled with hydrogen

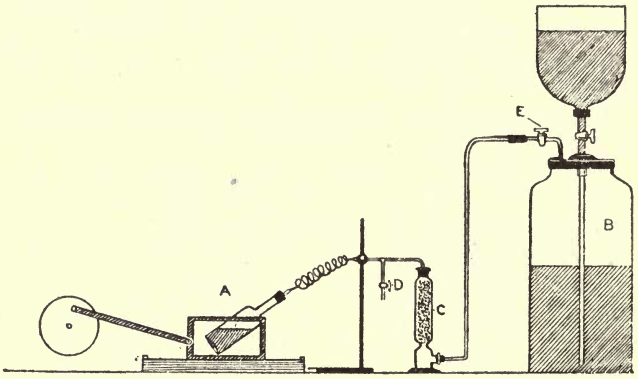


FIG. 3.

from the holder several times before starting an experiment.

The progress of absorption can be followed approximately by noting the diminution in volume of the hydrogen contained in *B*. Should the velocity of hydrogenation fall off unduly owing to the accumulation of gaseous impurities in the shaking vessel, the contents of this may be pumped out from time to time through *D*, fresh hydrogen being admitted through *E*. It is to be noted, however, that the velocity of absorption necessarily falls off as the saturation proceeds owing to the disappearance of

unsaturated molecules. Fokin[1] has shown that the course of the saturation with hydrogen of a double bond at constant temperature and pressure follows, as would be expected, the ordinary monomolecular formula :

$$K = \frac{1}{t} \log_e \frac{a}{a-x}.$$

in which a instead of being expressed in terms of unsaturated substance may conveniently be taken as the total volume of hydrogen absorbable by the weight of unsaturated body taken for treatment, x being the volume of hydrogen actually absorbed after time t.

For successful hydrogenation the necessity for hydrogen of the highest purity cannot be too strongly emphasised. A suitable gas may be prepared by electrolysis and subsequent elimination of the small percentage of oxygen usually present in such a gas (by passage over heated nickel or palladium) or, more conveniently, hydrogen of suitable purity may readily be bought in a compressed state in cylinders.

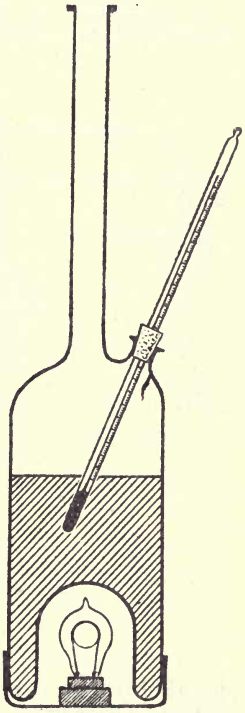


FIG. 4.

If the hydrogenation is to be carried out at an elevated temperature the reaction vessel is shaken in a bath maintained at the temperature required by means of an automatic thermo-regulator. It has also been proposed to heat the shaking vessel

[1] Fokin, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 276.

internally by means of a small electric lamp as shown in Fig. 4, a thermometer being inserted through the second neck.

Further, instead of employing a regular shaker it is also possible to obtain satisfactory results with a distilling flask provided with an efficient rotating stirrer, the apparatus being sealed off from

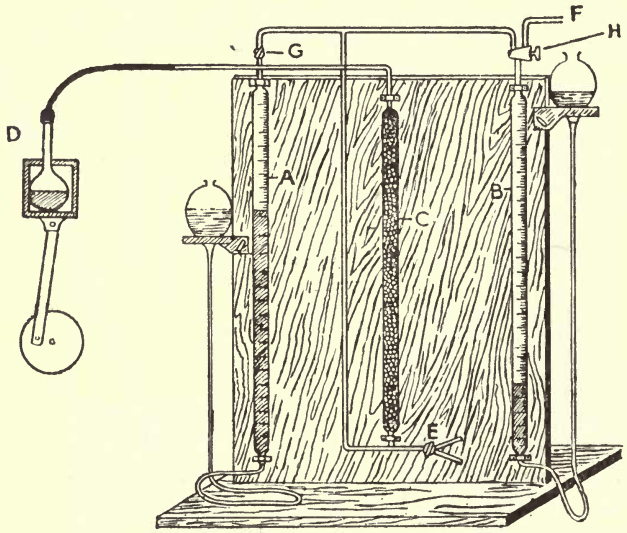


FIG. 5.

the air by means of liquid seals in the usual manner and attached to a supply of hydrogen. In this case, the air is of course displaced by means of a hydrogen current instead of by evacuation. An apparatus of this type has been employed by Reid[1] for the treatment of gases such as ethylene, the catalyst being suspended in paraffin or other inert liquid medium.

[1] Reid, *J. Amer. Chem. Soc.*, 1915, **37**, 2112.

The above types of apparatus admit of only a very approximate measurement of the volume of hydrogen absorbed, and for cases where it is necessary to follow more exactly the course of absorption the apparatus shown in Fig. 5 may be employed.

This consists of a gas burette, *A*, containing hydrogen and connected by way of the calcium chloride drying tube, *C*, to the shaking vessel, *D*. *B* is a hydrogen supply burette by means of which a known volume of hydrogen can be added to the system *A C D* as required.

To use the apparatus, the substance to be hydrogenated is mixed with catalyst and run into *D*, the connecting rubber or flexible copper tube being for this purpose removed and afterwards reconnected. *A* and *B* are filled with boiled water to the top of the taps *G* and *H*. The three-way tap, *E*, is then connected by means of its two branches to a vacuum and to a hydrogen supply respectively, and, *G* and *H* being closed, the system *A C D* is alternately evacuated and filled with hydrogen by operating the three-way tap, *E*.

After several evacuations and subsequent fillings, *G* is opened and hydrogen allowed to flow into it from the supply at *E*. As soon as *A* is filled down to the lower mark (250 c.c. is a convenient volume), *E* is closed and the hydrogen supply removed, *D* being, of course, not shaken up to this point. The filling being now complete, the hydrogen in the measuring burette, *A*, is adjusted to atmospheric pressure and its volume noted, this burette being placed in communication with the shaking vessel, and this latter being adjusted in its heating bath, if one is used. Shaking is now begun and the course of the absorption followed by noting the diminution of the volume of hydrogen in *A*, adjusted to atmospheric pressure by means of the water reservoir attached to it.

As soon as the gas in *A* is nearly absorbed, a

hydrogen supply is connected to F, and, by operating the three-way cock, H, a convenient amount is allowed to pass into B, the volume added being read off after adjusting levels. This known volume is now added to the system $A\,C\,D$ by turning H and raising the reservoir attached to B, that attached to A being temporarily lowered. Hydrogen is added to the system in this way from B from time to time as required by the absorption, the hydrogen

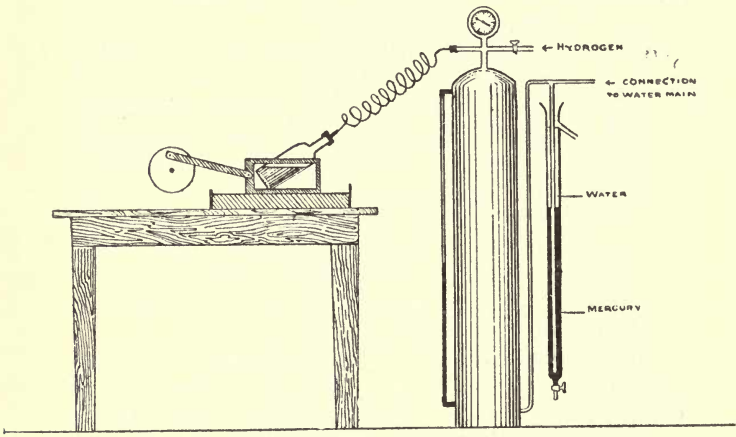


FIG. 6.

supply remaining connected to F during the whole of the experiment.

For work at an increased pressure, an apparatus designed by Skita and Meyer[1] and illustrated in Fig. 6, is to be recommended.

This consists of a closed copper vessel provided with a sight glass and a manometer, and connected to the shaking vessel by means of a flexible spiral copper tube. The hydrogen contained in the apparatus is maintained at an elevated pressure by

[1] Skita and Meyer, *Ber.*, 1912, **45**, 3379.

means of the head of water existing in the laboratory mains, and may be regulated as desired by interposing in the path of the water a mercury column of suitable height, arranged to act as a valve in that it releases the water in excess of that necessary for the maintenance of the pressure desired. The greater part of Skita's work with this apparatus was carried out at an excess pressure of about one atmosphere.

For work at higher pressure still, it is of course possible to connect a hydrogen cylinder provided with a reducing valve directly to a shaking vessel, which may, if the pressure is extremely high, be of copper instead of glass. Ipatiew has reduced many compounds at pressures up to 150 atmospheres in a stationary reaction vessel provided with a carefully-packed stirrer, but such high pressures are seldom required in practice.

The pressure employed plays, however, an important part, not only in directing the speed of the reaction, but even in deciding the nature of the product. This is particularly the case where easily reducible chains or rings are attached to nuclei which are less susceptible to reduction.

Many reactions, on the other hand, not only require no excess pressure for their successful realisation, but will even proceed in such a way that, if the hydrogen supply is cut off, a vacuum is produced by absorption of the gas present in the shaking vessel.

CHAPTER IV

The Hydrogenation of Unsaturated Chains

The preceding chapters of this book have dealt with the general methods of catalytic hydrogenation and with the preparation of suitable catalysts. Attention will now be paid to some of the results which have been obtained by the introduction of hydrogen into unsaturated molecules, this particular chapter being devoted to the saturation by hydrogen of ethylenic and acetylenic bonds between carbon atoms.

Unsaturated Hydrocarbons.

The simplest ethylenic hydrocarbon is ethylene itself. The hydrogenation of ethylene to ethane was described by Sabatier and Senderens[1] in 1897. Ethylene together with an excess of hydrogen was led at 35–40° C. over nickel, freshly reduced from the oxide at 300° C. A considerable rise in temperature takes place and ethane results.

A similar synthesis of ethane from ethylene and hydrogen, using other metals as catalysts, is described by Sabatier and Senderens in a later paper.[2] On passing the ethylene–hydrogen mixture over freshly reduced cobalt, a slight reaction was obtained even in the cold. This, however, soon stopped

[1] Sabatier and Senderens, *Compt. rend.*, 1897, **124**, 616.
[2] Sabatier and Senderens, *ibid.*, 1900, **130**, 1761.

owing to the deposition of a layer of carbon on the catalyst. At 100–150° C., in presence of nickel, the reduction takes place more readily, and this appears to be the most suitable temperature region for the reaction. At temperatures above 300° C. condensation and secondary products begin to be formed.

Finely divided copper does not begin to induce the reaction until 180° C. Between this and 300° C. the product consists of ethane, accompanied by only traces of methane and higher hydrocarbons. Iron, even when reduced below 400° C., is far less active than cobalt or copper. The reaction starts at 180° C., but soon stops on account of carbon deposition. Platinum black[1] was found to be active even at the ordinary temperature, but to lose this activity quickly owing to deposition of carbon. The most satisfactory reaction temperature is 180° C.

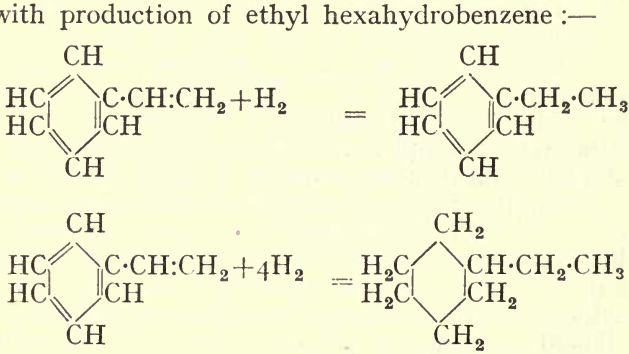
Propylene, and the higher ethylenic hydrocarbons generally, may easily be hydrogenated in a similar manner by leading the hydrocarbon in the gaseous state mixed with excess of hydrogen over finely divided nickel at 160° C.[2] At temperatures above 200° C. the hydrocarbon chain is ruptured, and the formation of simpler methane hydrocarbons and complex condensation products in small quantities is observed. In the case of hydrocarbons boiling at temperatures considerably above the atmospheric temperature, the hydrogenation may often be more conveniently carried out by the bubbling or shaking methods already described, using either colloidal platinum or palladium, or finely divided nickel at a higher temperature, as catalyst. The unsaturated body may also be dissolved in alcohol, ether, or glacial acetic acid, and saturated in the dissolved condition.

[1] Sabatier and Senderens, *Compt. rend.*, 1900, **131**, 40.
[2] Sabatier and Senderens, *ibid.*, 1902, **134**, 1137.

The reduction of ethylene and other unsaturated aliphatic hydrocarbons may also be carried out at the ordinary temperature in presence of colloidal palladium or platinum. Thus Paal and Hartmann[1] found that on shaking an aqueous solution of colloidal palladium, in presence of a protective colloid, with a mixture of equal volumes of hydrogen and ethylene contained in a gas burette, hydrogenation to ethane took place rapidly, accompanied by a contraction of the gas mixture to one-half its initial volume.

The hydrogenation of unsaturated side chains attached to aromatic nuclei, with or without the saturation of the aromatic nucleus itself, has also been effected. Thus, Sabatier and Senderens[2] found that by leading styrolene together with hydrogen over heated copper, ethyl benzene resulted, the ethylene portion only being reduecd.

On substituting nickel for copper the benzene nucleus in addition to the side chain was attacked, with production of ethyl hexahydrobenzene :—



The reduction of hydrocarbons containing more than one ethylenic linkage has been studied by Kelber and Schwarz,[3] who find that aromatic

[1] Paal and Hartmann, *Ber.*, 1909, **42**, 2239.
[2] Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 1254.
[3] Kelber and Schwarz, *Ber.*, 1912, **45**, 1946.

derivatives of butadiene are easily converted into compounds possessing a saturated aliphatic portion by hydrogen in presence of colloidal palladium protected from coagulation by " degraded " gluten.

Unsaturated Alcohols and Ethers.

The non-catalytic reduction of unsaturated alcohols by nascent hydrogen is often an operation of extreme difficulty, even the lower members of the series, such as allyl alcohol, being scarcely attacked. By means of hydrogen in presence of a catalyst, the ethylenic alcohols may without exception be easily reduced to the corresponding saturated compounds, and even, if desired, to the hydrocarbons themselves.

The most suitable catalysts are colloidal platinum or palladium, the operation being carried out in a shaker and stopped when the desired volume of hydrogen has been absorbed.

From allyl alcohol, normal propyl alcohol is obtained :

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH + H_2 = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH.$$

Similarly, crotonyl alcohol yields normal butyl alcohol.

Bouveault and Blanc[1] studied the reduction of some higher unsaturated alcohols in presence of non-colloidal platinum black. The saturation of these higher alcohols seems to be accompanied by the reduction of the hydroxyl group, saturated hydrocarbons being obtained in addition to the corresponding saturated alcohol. From oleic alcohol Bouveault and Blanc prepared octadecyl alcohol, $C_{18}H_{37}{\cdot}OH$, and from erucyl alcohol docosyl alcohol, $C_{22}H_{45}{\cdot}OH$.

[1] Bouveault and Blanc, *Bull.*, 1904 (3), **31**, 1210.

$$\underset{\text{Oleic alcohol.}}{CH_3(CH_2)_7\cdot CH{:}CH(CH_2)_8\cdot OH} + H_2 = \underset{\text{Octadecyl alcohol.}}{CH_3(CH_2)_{17}\cdot OH}$$

$$\underset{\text{Erucyl alcohol.}}{CH_3(CH_2)_7\cdot CH{:}CH(CH_2)_{12}\cdot OH} + H_2 = \underset{\text{Docosyl alcohol.}}{CH_3(CH_2)_{21}\cdot OH},$$

The hydrogenation of some higher secondary ethylenic alcohols was undertaken by R. Douris[1] at 195–200° C. in presence of nickel. He found that, at this high temperature, very little, if any, of the corresponding saturated alcohol was obtained, the reaction proceeding as far as the corresponding saturated hydrocarbon.

The alcohols studied included propenyl isoamyl carbinol,

$$CH_3\cdot CH{:}CH\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH(CH_3)_2,$$

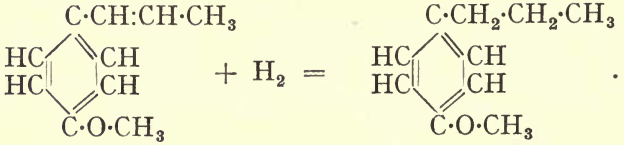
and vinyl isobutyl carbinol,

$$CH_2{:}CH\cdot CH(OH)\cdot CH_2\cdot CH(CH_3)_2.$$

Douris found that the reaction product always contained a saturated ketone, formed by intramolecular change thus :

$$R\cdot CH{:}CH\cdot CH(OH)\cdot R = R\cdot CH_2\cdot CH_2\cdot CO\cdot R.$$

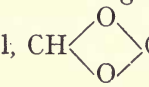
Ipatiew,[2] working with nickel at 95° C. (3 grams of nickel in 30 grams of anethol) under a hydrogen pressure of 50 atmospheres, succeeded in hydrogenating anethol to the dihydro-compound in four hours :

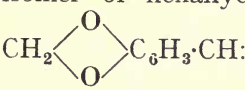


[1] R. Douris, *Compt. rend.*, 1913, **157**, 55.
[2] Ipatiew, *Ber.*, 1913, **46**, 3589.

By continuing the hydrogenation at 200° C. for twenty hours, hexahydropropyl benzene was formed, a methoxy-group being split off.

Similarly, eugenol, $CH_3O{\cdot}C_6H_3(OH){\cdot}CH_2{\cdot}CH{:}CH_2$, was reduced to dihydroeugenol in presence of nickel at 95° C. On raising the temperature to 195° C. and continuing the reduction for seven hours longer, a mixture of hexahydroanethol and octahydroeugenol was obtained. Isoeugenol, on being reduced with nickel for two hours at 95° C., yielded the normal dihydro-compound identical with that obtained from eugenol.

Safrol,  , was similarly reduced to the dihydro-compound by the introduction of two hydrogen atoms into its side chain in presence of nickel at 95° C., working for two hours in a pressure apparatus.

On raising the temperature to 180° C. and continuing the reduction, oxygen was split off and an isomer of hexahydroanethol produced. Isosafrol,  , yielded, as would be expected, a dihydro-product indentical with that obtained from safrol.

The hydrogenation of geraniol has been studied by Willstätter[1] and by Enklaar,[2] using platinum or palladium as a catalyst.

Aldehydes and Ketones.

The hydrogenation in presence of colloidal palladium of acrolein, the simplest olefinic aldehyde, has been investigated by Skita.[3] In addition to the normal hydrogenation product, propionic aldehyde,

[1] Willstätter, *Ber.*, 1908, **41**, 1478.
[2] Enklaar, *ibid.*, 1908, **41**, 2084.
[3] Skita, *ibid.*, 1912, **45**, 3312.

some allyl alcohol, resulting from the reduction of the aldehydic group, was obtained.

$$CH_2{:}CH{\cdot}CHO + H_2 = CH_3{\cdot}CH_2{\cdot}CHO$$
$$CH_2{:}CH{\cdot}CHO + H_2 = CH_2{:}CH{\cdot}CH_2{\cdot}OH$$

Various unsaturated ketones and aldehydes have been reduced by Ipatiew with hydrogen under high pressure, methyl ethyl acrolein, for instance, being converted into methyl isobutyl ketone, while mesityl oxide gave a mixture of methyl isobutyl ketone and carbinol:

$$\underset{\text{Mesityl oxide.}}{CH_3{\cdot}CO{\cdot}CH{:}C(CH_3)_2} + H_2 = \underset{\text{Methyl isobutyl ketone.}}{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH(CH_3)_2}$$

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH(CH_3)_2 + H_2 = \underset{\text{Methyl isobutyl carbinol.}}{CH_3{\cdot}CH{\cdot}OH{\cdot}CH_2{\cdot}CH(CH_3)_2}$$

Skita[1] has since obtained a similar result with methyl ethyl acrolein at the ordinary pressure in presence of palladium.

The hydrogenation of aldehydes and ketones containing several ethylenic linkages has been described by Borsche,[2] who states that, in general, when working according to Paal's method, highly unsaturated ketones containing one double linkage on each side of the CO group are easily converted with a good yield into the corresponding saturated body. If, however, either side of the CO group contains more than one double linkage, the yield of the normal reduction product is diminished very considerably by the formation of resinous bodies.

Thus dibenzal acetone,

$$C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_5,$$

is capable of easy and quantitative reduction. With cinnamal acetophenone,

$$C_6H_5{\cdot}CO{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C_6H_5,$$

[1] Skita, *Ber.*, 1915, **48**, 1486. [2] Borsche, 1912, *ibid.*, **45**, 46.

and still more so with benzal cinnamal acetone,

$$C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C_6H_5,$$

side reactions occur.

Skita,[1] using colloidal palladium in alcoholic solution, with gum arabic as a protective colloid, reduced phorone by the addition of 6 atoms of hydrogen to di-isobutyl carbinol while isophorone was converted into dihydroisophorone.

Ipatiew[2] succeeded in preparing the saturated alcohol decanol by the reduction of citral. Skita[3] had previously only been able to hydrogenate citral to a mixture of citronellal and citronellol, one double bond being left unsaturated :

$$(CH_3)_2{\cdot}C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\displaystyle CH_3}{\overset{|}{C}}{:}CH{\cdot}CHO + H_2 =$$

Citral.

$$CH_2{:}\overset{\displaystyle CH_3}{\overset{|}{C}}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\displaystyle CH_3}{\overset{|}{C}}{\cdot}CH_2{\cdot}CHO$$

Citronellal.

$$(CH_3)_2{\cdot}C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\displaystyle CH_3}{\overset{|}{C}}{:}CH{\cdot}CHO + 3H_2 =$$

Citral.

$$(CH_3)_2{\cdot}CH(CH_2)_3{\cdot}\overset{\displaystyle CH_3}{\overset{|}{C}}{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$

Decanol.

Acids and Esters.

While the lower unsaturated fatty acids such as acrylic acid are attacked more or less readily by nascent hydrogen, the higher members of the series, on the other hand, are not affected. It is

[1] Skita, 1909, *Ber.*, **42**, 1630. [2] Ipatiew, 1912, *ibid.*, **45**, 3218. [3] Skita, *loc. cit.*

for this reason that the commercial manufacture of stearic acid from oleic acid only became possible after Sabatier's work on the activation of free gaseous hydrogen by nickel and other metals. The so-called hardening of technical fats and oils will receive special attention in a later chapter, and it is therefore proposed to deal here only with the laboratory side of the question.

The unsaturated fatty acids are as a class extremely easily hydrogenated by any of the methods already described. This applies also to the unsaturated dibasic acids and to unsaturated acid chains attached to an aromatic nucleus. Thus, employing colloidal metals of the platinum group as catalyst Paal and Gerum[1] reduced fumaric, maleic and cinnamic acids to the corresponding saturated compounds.

Paal's method of hydrogenation of the sodium salts in aqueous solution has been extended by Böeseken, van der Weide and Mom[2] to acids such as crotonic, cinnamic, sorbic, and undecylenic. These investigators found further that an accumulation of carboxyl groups round the unsaturated linkage impeded hydrogenation.

Oleic acid in ethereal solution was reduced to stearic acid by Fokin[3] with platinum metal catalysts, a 90 per cent. yield of stearic acid being reported. R. Willstätter[4] effected a more rapid reduction of oleic acid, using platinum black prepared according to Löw's method.[5]

The use of hydrosols of the platinum metals was introduced by Paal and Roth,[6] who hydro-

[1] Paal and Gerum, *Ber.*, 1908, **41**, 2273.
[2] Böeseken, van der Weide, and Mom, *Rec. trav. chim. Pays-Bas*, 1916, **35**, 260.
[3] Fokin, *Chem. Centralblatt*, 1906 (ii), 758; 1907, (i), 324, (ii), 1324.
[4] Willstätter, *Ber.*, 1908, **41**, 1475.
[5] Löw, *ibid.*, 1890, **23**, 289.
[6] Paal and Roth, *ibid.*, 1908, **41**, 2282.

genated in this way both the alkali salts of the fatty acids and the natural fats. Castor oil was reduced by these investigators in alcoholic solution; olive and fish oils in the form of an emulsion with water, containing a little gum arabic as a protective colloid. In a later paper[1] a similar hydrogenation of croton, sesame, cotton and linseed oils, also butter fat and lard, is described.

It is not, however, necessary to dissolve the unsaturated fatty acid or glyceride in any way. A satisfactory method of carrying out the hydrogenation on a laboratory scale is to mix intimately with the oil or other substance sufficient finely powdered platinum or palladium oxide or palladium chloride to give on reduction 0·1 gram of platinum or palladium for every 100 grams of the oil. The oil and catalyst are either treated in a shaker in the usual way or hydrogenated by simple passage of a rapid current of hydrogen, this operation being with advantage carried out at a temperature of 100° C. or even higher.

If it is desired to use nickel as a catalyst, this may be reduced from oxide and added to the oil in the proportion of about 1 per cent., the hydrogenation being carried out at about 200° C. or lower if desired. The nickel oxide may also be added as such to the oil and the hydrogenation carried out by passing a rapid current of hydrogen through the mixture heated to 250–260° C. in an oil-bath according to Bedford and Williams's method. For fatty acids which are easily volatile in a current of hydrogen, Sabatier's vapour method of treatment may well be used.

Borsche[2] has obtained various new or difficultly prepared acids containing several double bonds. δ-Phenyl valeric acid was prepared from cinnamenyl

[1] Paal and Roth, *Ber.*, 1909, **42**, 1541.
[2] Borsche, *ibid.*, 1912, **45**, 620.

acrylic acid, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}COOH$; phenyl *n*-propyl malonic acid,

$$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOH)_2,$$

from cinnamal malonic acid,

$$C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}C(COOH)_2.$$

On heating this saturated acid, carbon dioxide was given off and phenyl valeric acid produced.

Similarly, *ω*-phenyl *n*-propyl cyanacetic acid was obtained from cinnamal cyanacetic acid, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}C(CN){\cdot}COOH$, *aδ*-diphenyl valeric acid from cinnamal phenyl acetic acid, and *aδ*-diphenyl valeric nitrile from cinnamal benzyl cyanide, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}C(C_6H_5){\cdot}CN$.

The hydrogenation of various highly unsaturated bodies, including cinnamal malonic acid, has also been studied by Paal.

Reduction of Unsaturated Halogen Compounds.

Attempts to obtain the corresponding saturated halogen bodies have not been successful with certain aromatic derivatives of ethylene, the hydrogenation of which was investigated by Borsche and Heimbürger.[1] *ω*-Bromostyrolene, for instance, was found to pass by hydrogenation and elimination of hydrobromic acid into ethyl benzene, while methylene dioxy-*ω*-chlorostyrolene gave the methylene ether of ethyl pyrocatechin :—

ω-Bromostyrolene. Ethyl benzene.

The Saturation of Acetylenic Bonds.

Acetylene and its homologues, as a class, combine with free or nascent hydrogen even more readily than the olefines.

[1] Borsche and Heimbürger, *Ber.*, 1915, **48**, 452.

The hydrogenation of acetylene itself to ethane in presence of platinum black was described in 1874 by de Wilde.[1] Sabatier and Senderens,[2] working later on the same subject, found that copper, cobalt, iron, and, above all, nickel could be substituted for the platinum black, but that the energy of the reaction, combined with the endothermic nature of acetylene, led to the formation of polymeric products and to the liberation of free carbon. These phenomena also resulted by leading acetylene alone over various finely divided metals, hydrogen being absent.[3] The hydrogenation begins with platinum black at the ordinary temperature, with nickel at about 100° C., while copper, iron, and cobalt require temperatures lying between 130° C. and 200° C.

A more satisfactory reaction, accompanied by a quantitative yield and absence of by-products, may be obtained by shaking a mixture of hydrogen and acetylene with an aqueous suspension of colloidal platinum or palladium.

A further and interesting example of the comparative activity of nickel and copper is furnished by the hydrogenation of amyl acetylene.[4] By passage, mixed with excess of hydrogen, over copper at 180° C., normal amyl ethylene was produced,

$$CH_3{\cdot}(CH_2)_4{\cdot}C{:}CH + H_2 = CH_3{\cdot}(CH_2)_4{\cdot}CH{:}CH_2,$$

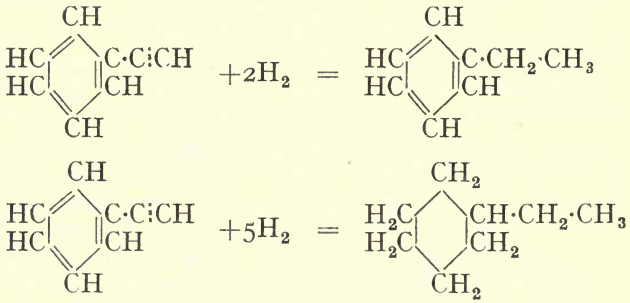
while nickel was found to give the saturated paraffin heptane,

$$CH_3{\cdot}(CH_2)_4{\cdot}C{:}CH + 2H_2 = CH_3{\cdot}(CH_2)_5{\cdot}CH_3.$$

A somewhat similar differentiation was obtained

[1] De Wilde, *Ber.*, 1874, **7**, 353.
[2] Sabatier and Senderens, *Compt. rend.*, 1899, **128**, 1173; 1900, **130**, 1559, 1628; 1900, **131**, 40.
[3] Sabatier and Senderens, *ibid.*, 1897, **124**, 616; 1900, **130**, 250; 1900, **131**, 187, 267.
[4] Sabatier and Senderens, *ibid.*, 1902, **135**, 87.

with phenyl acetylene, this being reduced in presence of copper at 180° C. to ethyl benzene, or, in presence of nickel, to ethyl cyclohexane, the benzene ring being in this case also attacked :



Paal and Hohenegger [1] find that the hydrogenation of acetylene in presence of colloidal palladium is complicated by adsorption of acetylene by the palladium, so that the hydrogen, which was added only in volume calculated to produce ethylene, was really in effective excess, ethane resulting. It was found, however, that by using colloidal palladium which had already been treated with acetylene and had thus lost its power of adsorbing the gas, a reaction product consisting almost entirely of ethylene is produced. With colloidal platinum (Paal and Schwarz [2]) adsorption of acetylene is less pronounced but hydrogenation proceeds more slowly and less completely than with palladium.

The hydrogenation in stages of aromatic substitution products of acetylene has been studied by Kelber and Schwarz.[3] Two grams of phenylacetylene, dissolved in 5 c.c. of glacial acetic acid together with 0·1 c.c. of colloidal palladium in 10 c.c. of glacial acteic acid, were reduced after several

[1] Paal and Hohenegger, *Ber.*, 1915, **48**, 275.
[2] Paal and Schwarz, *ibid.*, 1915, **48**, 1202.
[3] Kelber and Schwarz, *ibid.*, 1912, **45**, 1946.

hours' hydrogenation in a shaker at the ordinary temperature first to styrolene, then to ethyl benzene, the yield being almost quantitative :

$$\underset{\text{Phenyl acetylene.}}{C_6H_5\cdot C{:}CH} + H_2 = \underset{\text{Styrolene.}}{C_6H_5\cdot CH{:}CH_2}$$

$$C_6H_5\cdot CH{:}CH_2 + H_2 = \underset{\text{Ethyl benzene.}}{C_6H_5\cdot CH_2\cdot CH_3}$$

Similarly, tolane was found to pass into iso-stilbene and finally into di-benzyl,

$$C_6H_5\cdot C{:}C\cdot C_6H_5 \rightarrow C_6H_5\cdot CH{:}CH\cdot C_6H_5 \rightarrow C_6H_5\cdot CH_2\cdot CH_2\cdot C_6H_5,$$

while from diphenyl diacetylene a mixture of about 25 per cent. of cis-cis-$a\delta$-diphenyl-$a\gamma$-butadiene and 75 per cent. of cis-trans-$a\delta$-diphenyl-$a\gamma$-butadiene and finally a quantitative yield of $a\delta$-diphenylbutane was obtained :

$$\underset{\text{Diphenyldiacetylene.}}{C_6H_5\cdot C{:}C\cdot C{:}C\cdot C_6H_5} \qquad \underset{\text{Diphenylbutadiene.}}{C_6H_5\cdot CH{:}CH\cdot CH{:}CH\cdot C_6H_5}$$

$$\underset{\text{Diphenylbutane.}}{C_6H_5\cdot (CH_2)_4\cdot C_6H_5}$$

The ease of reduction of the acetylenic union renders possible the use of non-colloidal catalysts, even for reactions carried out in a shaker at the ordinary temperature.

Finally, Lespieau and Vavon[1] reduced di-allylene dicarboxylic acid containing two acetylenic bonds to suberic acid in presence of platinum black :

$$\underset{\text{Diallylene dicarboxylic acid.}}{\begin{matrix} CH_2\cdot C{:}C\cdot COOH \\ | \\ CH_2\cdot C{:}C\cdot COOH \end{matrix}} + 4H_2 = \underset{\text{Suberic acid.}}{\begin{matrix} CH_2\cdot CH_2\cdot CH_2\cdot COOH \\ | \\ CH_2\cdot CH_2\cdot CH_2\cdot COOH \end{matrix}}$$

[1] Lespieau and Vavon, *Compt. rend.*, 1909, **148**, 1331.

CHAPTER V

The Hydrogenation of Unsaturated Rings

It is particularly in connection with the reduction of benzene and other cyclic bodies that catalytic hydrogenation has opened a way for the easy preparation of saturated bodies which were otherwise difficult to obtain. Thus hexahydrobenzene, which had hitherto only been obtained directly in small yield by the action of hydriodic acid on benzene at high temperatures, or indirectly by means of a series of complicated reactions from *p*-ketohexamethylene, as demonstrated by the classical work of A. von Baeyer, was prepared by Sabatier and Senderens with the greatest ease by leading the vapours of benzene mixed with hydrogen over a nickel catalyst.

The hydrogenation of an unsaturated ring is in general an endothermic process and takes place with less readiness than the saturation of an ethylenic or acetylenic linkage, the reaction being in the case of the last two classes of bodies accompanied by a considerable evolution of heat. Thus the technical "hardening" of oils, an operation which is carried out under conditions for preventing loss of heat during reaction, may be accompanied by a rise in temperature of as much as 50° C. or even more (see Chapter VIII). This difference has already been the subject of comment in connection with the saturation of styrolene, under the influence of nickel and of the less energetic catalyst copper.

It may further be noted that Ipatiew, in studying the effect of hydrogen under pressure on substances containing both an ethylenic bond and an unsaturated benzene ring, using copper as a catalyst, found that whereas the ethylenic bond was hydrogenated at 270–300° C., the benzene nucleus remained unattacked. When nickel was substituted for copper it was found that an addition of hydrogen to the ethylenic linkage took place at 95° C., while for the hydrogenation of the benzene ring a temperature of 185–190° C. was necessary.

Hydrogenation of the Benzene Ring.

As has already been mentioned, the direct hydrogenation of benzene in presence of a nickel catalyst was first carried out by Sabatier and Senderens.[1]

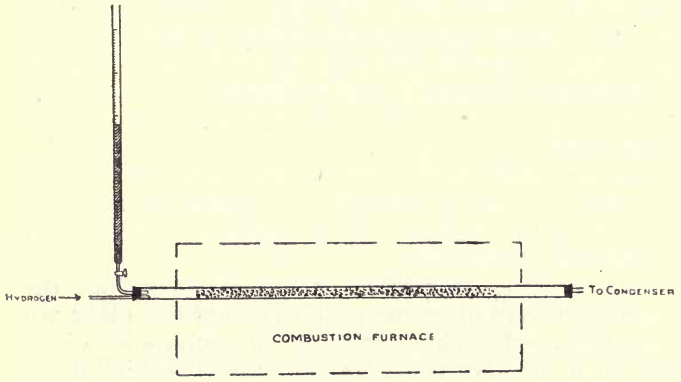


FIG. 7.

Benzene, mixed with excess of hydrogen, is passed over a layer of freshly reduced nickel contained in a glass, or, better, silica tube. The reaction takes place with appreciable velocity at 180° C., and

[1] Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 210, 566, 1254.

appears to proceed most satisfactorily at about 250° C. Above 300° C. reversal (dehydrogenation) sets in, hexahydrobenzene being reconverted to benzene.

The reaction may well be carried out in the apparatus already described for hydrogenation by the " vapour " method (see Fig. 1). Sabatier and Senderens's original apparatus is illustrated in Fig. 7.

The nickel catalyst employed remains active for a considerable time, whereas Sabatier and Senderens state that cobalt and platinum black lose their activity after a few minutes' use, while iron, copper, and platinum sponge were found by them to be inactive.

The reduction of benzene to hexahydrobenzene in a shaker at the ordinary temperature has been studied by Willstätter and Hatt.[1] Using as a catalyst non-colloidal platinum, prepared by Löw's method, these investigators found that while commercially " pure " benzene (containing traces of thiophene) absorbed no hydrogen, pure benzene was quantitatively reduced to the hexahydro-compound.

Under the conditions employed, 1 gram of benzene absorbed in the presence of 0·6 gram of platinum the theoretical volume of hydrogen for hexahydrobenzene in seven hours.

By working in glacial acetic acid solution, the reduction took place more quickly and less platinum could be used. Thus 3·7 grams of benzene dissolved in 5 c.c. of glacial acetic acid and containing 0·4 gram of platinum were hydrogenated completely after shaking for six hours. The addition of even a trace of thiophene to pure benzene was found to stop the reaction completely. Henrichsen and Kaempf[2] report, however, that caoutchouc is non-poisonous for the reaction.

[1] Willstätter and Hatt, *Ber.*, 1912, **45**, 1471.
[2] Henrichsen and Kaempf, *ibid.*, 1912, **45**, 2106.

Ipatiew[1] investigated the reduction of benzene by hydrogen under high pressure in presence of nickel oxide. Working with 2·5 grams of benzene and 2 grams of nickel oxide, reduction to hexahydrobenzene was obtained in 1½ hours at 250° C., the hydrogen pressure being 150–200 atmospheres. Iron was found to be inactive for the reaction.

Toluene, xylene, cymene, and other homologues of benzene are reduced with equal or even with greater ease than benzene itself, both by the vapour method and by treatment with hydrogen in a shaker. Sabatier and Senderens state, however, that the presence of long side-chains is liable to lead to decomposition and to side reactions. Willstätter and Hatt found that the cheapest form of toluene absorbed hydrogen even more rapidly than pure benzene. For instance, 1·8 grams of toluene dissolved in 3 grams of glacial acetic acid, after treatment in a shaker in presence of 0·5 gram of platinum, absorbed in 3½ hours the theoretical volume of hydrogen for conversion into hexahydrotoluene, the temperature being 20° C. and the pressure 725 mm.

Similar results were obtained with xylene and with durene. Six grams of xylene with 0·9 gram of platinum absorbed in one day at 20° C. a volume of hydrogen equivalent to complete conversion into hexahydroxylene. Pure durene was found to be soluble with difficulty in glacial acetic acid and was treated as a suspension in this medium. Two grams of durene suspended in 12 grams of glacial acetic acid were quantitatively hydrogenated in six hours at 20° C.

The hydrogenation of benzene and toluene in glacial acetic acid in presence of colloidal platinum, and of gum arabic as a protective colloid, has been described by Skita and Meyer,[2] normal reduction products being obtained.

[1] Ipatiew, *Ber.*, 1907, **40**, 1281.
[2] Skita and Meyer, *ibid.*, 1912, **45**, 3579.

Of other hydrocarbons derived from benzene, diphenyl has been the subject of several investigations. Eijkman,[1] who first studied the reduction of this compound by the vapour method in presence of nickel, obtained only the semi-hydrogenated $C_6H_{11}\cdot C_6H_5$. Sabatier and Murat[2] found that if the vapours of diphenyl are led over nickel at 180° C. together with a large excess of hydrogen, phenylcyclohexane is formed, as above, without an appreciable quantity of dicyclohexyl. If, however, the reaction product be further hydrogenated in the presence of nickel at 160° C., dicyclohexyl is produced.

The varied reduction of styrolene in presence of nickel and of copper has already been discussed.

The hydrogenation of the tetra-ring body cyclobutene in presence of nickel was found by Willstätter and Bruce[3] to proceed normally at 100° C. with formation of cyclobutane. At 200° C., however, reduction proceeded to butane, the ring being ruptured.

Cyclobutene. Cyclobutane.

Hydrogenation of Naphthalene.

The direct hydrogenation of naphthalene by distillation over nickel at 200° C. was first described by Sabatier and Senderens.[4]

Willstätter and Hatt[5] state that purest commercial naphthalene cannot be hydrogenated in a

[1] Eijkman, *Chem. Weekblad.*, 1903, **1**, 7.
[2] Sabatier and Murat, *Compt. rend.*, 1912, **154**, 1390.
[3] Willstätter and Bruce, *Ber.*, 1907, **40**, 3979.
[4] Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 1254.
[5] Willstätter and Hatt, *Ber.*, 1912, **45**, 1471.

shaker, even when dissolved in glacial acetic acid, on account of its sulphur content. It may be obtained sufficiently pure for reaction by about twelve recrystallisations from acetone, alcohol, or glacial acetic acid. For the preparation of naphthalene in a still purer condition, the above authors recommend the following indirect method.

Pure *a*-naphthylamine is converted into the hydrazine derivative, the hydrochloride of which is recrystallised and the base distilled off in a vacuum. By oxidation with copper sulphate the hydrocarbon is obtained pure enough readily to absorb hydrogen in presence of platinum, the decahydro-derivative being produced.

Willstätter and Hatt found that the reaction was three times as rapid in glacial acetic acid as in ethereal solution. 0·9 Gram of naphthalene in 6 grams of ether with 0·5 gram of platinum was completely reduced after 15 hours' shaking, while 6 grams of naphthalene in 65 grams of glacial acetic acid with 2·5 grams of platinum required five hours only.

Naphthalene is also readily hydrogenated in presence of colloidal platinum or palladium.

The hydrogenation of naphthalene to the decahydro-body has also been carried out by Leroux.[1]

Anthracene and other poly-ring hydrocarbons may be reduced under conditions similar to those described for naphthalene. Anthracene was reduced to tetrahydroanthracene by Godchot[2] in presence of nickel at 250° C. On effecting the reduction at 200° C., octahydroanthracene was formed.

The hydrogenation of phenanthrene has been studied by Breteau.[3] In the presence of nickel at 160° C., using the vapour method, phenanthrene was converted into a mixture of tetrahydro- and octa-

[1] Leroux, *Compt. rend.*, 1904, **139**, 672.
[2] Godchot, *ibid.*, 1904, **139**, 604.
[3] Breteau, *ibid.*, 1910, **151**, 1368.

hydro-phenanthrene. On dissolving phenanthrene in hexahydrobenzene and hydrogenating in this solvent in presence of platinum, the pure tetrahydro-compound was obtained.

J. Schmidt and E. Fischer [1] find that phenanthrene may be quantitatively reduced to 9 : 10–dihydro-phenanthrene by dissolving in ether and refluxing in the presence of platinum black, hydrogen being passed through the liquid.

Phenanthrene. 9 : 10-Dihydrophenanthrene.

Reduction of Rings containing a Higher Number of Carbon Atoms.

Willstatter [2] and his pupils have paid considerable attention to the hydrogenation of cyclo-octene to cyclo-octane. Nickel is stated to be unsuitable even at low temperatures owing to side reactions. By using platinum black, pure cyclo-octane was obtained. Similarly, dimethylgranatanine was reduced to dimethylaminocyclo-octane.

The reduction of other ring bodies in presence of nickel oxide at a high pressure has been studied by Ipatiew.[3] Fluorene after treatment with hydrogen at 120 atmospheres at a temperature of 290° C. passed into decahydrofluorene, acenaphthene successively into the tetrahydro- and decahydro-derivatives, while retene gave decahydroretene.

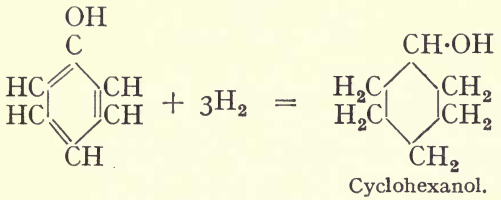
[1] J. Schmidt and E. Fischer, *Ber.*, 1908, **41**, 4225.

[2] Willstätter and Wäser, *ibid.*, 1910, **43**, 1176; Willstätter and Veraguth, *ibid.*, 1907, **40**, 957; Willstätter and Kametaka, *ibid.*, 1908, **41**, 1480.

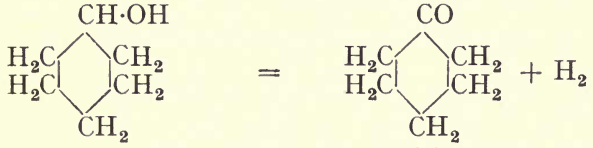
[3] Ipatiew, *ibid.*, 1909, **42**, 2092.

Reduction of Phenols.

Phenol vapour, passed, together with hydrogen, over nickel at 200–300° C. is reduced to cyclohexanol, which by loss of hydrogen passes into cyclohexanone.[1]



Cyclohexanol.



Cyclohexanone.

Pure cyclohexanol is obtained by reduction of phenol with hydrogen in presence of nickel at 140–150° C. On treating cyclohexanol with copper at 300° C. in absence of hydrogen, pure cyclohexanone is formed.

Skita and Ritter[2] found that by distilling mixtures of phenol and hydrogen over nickel considerable decomposition took place, cyclohexanone, hexahydrobenzene, and tetrahydrobenzene being formed according to conditions. From *m*-cresol, hexahydrotoluol and methylcyclohexanone were obtained.

Cyclohexanone was found to pass into cyclohexane and by dehydrogenation into phenol. It appears, therefore, that the direct hydrogenation of phenol by the vapour method is extremely liable to be accompanied by side reactions—an effect which is in

[1] Sabatier and Senderens, *Compt. rend.*, 1903, **137**, 1025.
[2] Skita and Ritter, *Ber.*, 1912, **45**, 668.

general not obtained in a shaker, especially at the ordinary temperature. The direct hydrogenation of polyphenols to hexahydro-compounds by the vapour method at 130° C. has also been studied by Sabatier and Mailhe.[1]

Acids and Esters.

Benzoic acid was found by Skita and Meyer[2] to absorb 6 atoms of hydrogen when treated in a shaker in presence of colloidal platinum or palladium, hexahydrobenzoic acid being produced.

The hydrogenation of benzoic esters by distillation over nickel is described by Sabatier and Murat.[3] On leading methyl benzoate together with hydrogen over nickel at 210–225° C. some reduction was obtained, but the fixation of hydrogen was soon stopped by deposition of a thin film of benzoate over the surface of the nickel. However, on carrying out the reaction at 180° C. and employing a large excess of hydrogen, the hexahydro-reduction product resulted and the hydrogenation proceeded smoothly. In a similar manner, Sabatier and Murat succeeded in preparing hexahydro-compounds from ethyl and isoamyl benzoates.

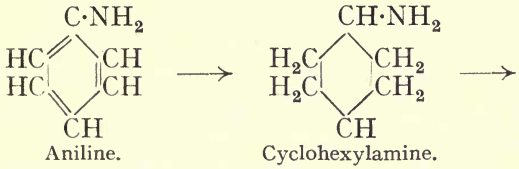
Zelinski and Glinka[4] hydrogenated tetrahydroterephthalic ester, a mixture of the normal hexahydroterephthalic ester and a hydroxy-compound being obtained.

Various Aromatic Derivatives.

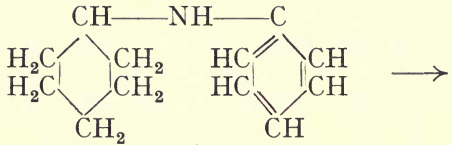
Aniline, led with hydrogen over nickel at 190° C. is converted into a mixture of cyclohexylamine,

[1] Sabatier and Mailhe, *Compt. rend.*, 1908, **146**, 1193.
[2] Skita and Meyer, *Ber.*, 1912, **45**, 3579.
[3] Sabatier and Murat, *Compt. rend.*, 1912, **154**, 922.
[4] Zelinski and Glinka, *Ber.*, 1911, **44**, 2305.

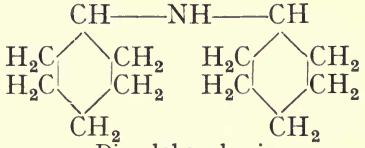
dicyclohexylamine, and cyclohexylaniline,[1] analogous results being obtained with diphenylamine.



Aniline. Cyclohexylamine.



Cyclohexylaniline.

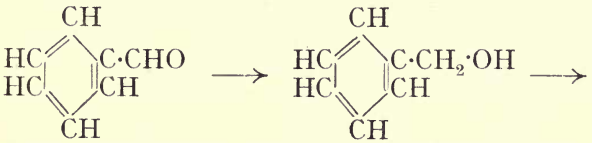


Dicyclohexylamine.

Methyl and ethyl aniline behave similarly.[2]

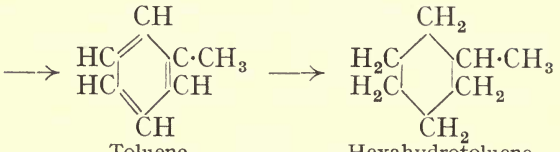
An interesting variation in the hydrogenation of benzaldehyde has been recorded by Skita.[3]

Using platinum as a catalyst, this passed in alcoholic solution to benzyl alcohol, in acetic acid solution at ordinary pressure to toluene, and, at a pressure of three atmospheres, to hexahydrotoluene.



Benzaldehyde. Benzyl alcohol.

[1] Sabatier and Senderens, *Compt. rend.*, 1904, **138**, 457.
[2] Sabatier and Senderens, *ibid.*, 1904, **138**, 1257.
[3] Skita, *Ber.*, 1915, **48**, 1486.

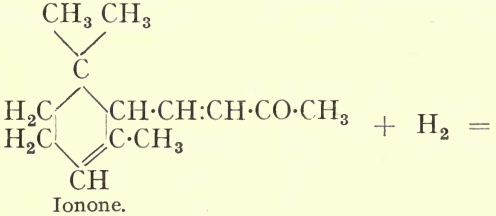


Toluene, Hexahydrotoluene.

Sabatier and Mailhe[1] on attempting to hydrogenate chlorobenzene by the vapour method in presence of nickel obtained only decomposition products. The same authors[2] found that aromatic quinones and diketones under similar conditions underwent reduction of their carbonyl groups without appreciable hydrogenation of the benzene ring.

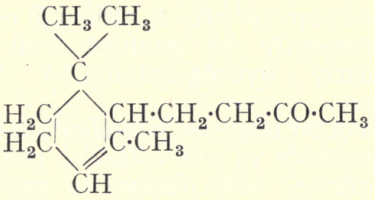
Reduction of Terpenes.

We may well consider at this point the hydrogenation of various terpenic compounds. Skita[3] studied the action of hydrogen, at the ordinary temperature in the presence of palladium, on the ionones. 9·6 Grams of *α*-ionone, 0·01 gram of palladium chloride and 0·01 gram of gum arabic were dissolved in a mixture of 100 c.c. of alcohol and 50 c.c. of water. The ionone was converted after shaking for forty-five minutes, at an increased pressure of one atmosphere, to dihydro-ionone, and after seventy-five minutes to the tetrahydro-compound. *β*-Ionone behaved similarly.

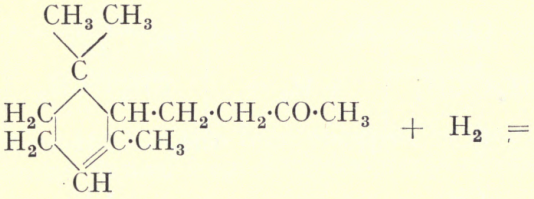


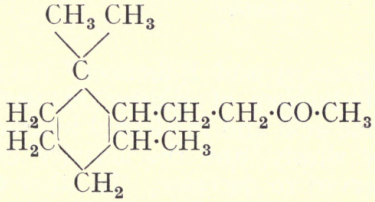
Ionone.

[1] Sabatier and Mailhe, *Compt. rend.*, 1904, **138**, 245.
[2] Sabatier and Mailhe, *ibid.*, 1907, **145**, 1126; 1908, **146**, 457.
[3] Skita, *Ber.*, 1912, **45**, 3312.



Dihydro-ionone.





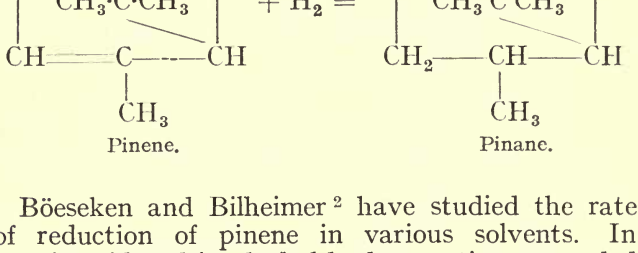
Tetrahydro-ionone.

It will be noticed that in each case it is the extra-cyclic double bond which first of all becomes saturated. The odour of ionone disappeared with the saturation of the first double bond. It may be mentioned that Skita succeeded in preparing, by a condensation method, a dihydro-ionone saturated in the ring but containing an ethylenic linkage. This body possessed a smell reminiscent of ionone.

All the ionone reductions given above are characterised by the fact that the CO group is left untouched. *α*- and *β*-Ionones give isomeric dihydro-compounds but identical tetrahydro-derivatives.

Pseudo-ionone (which, although not a ring body may conveniently be grouped with the ionones) is similarly hydrogenated to tetrahydro-pseudo-ionone.

Of other terpenes, camphor has been hydrogenated in presence of non-colloidal platinum to dihydro-camphene, and pinene, in presence of colloidal platinum, to pinane.[1]

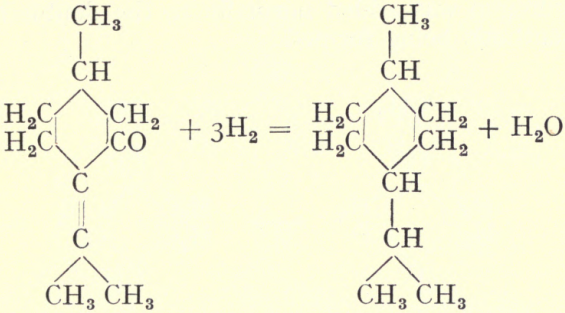


Pinene. Pinane.

Böeseken and Bilheimer[2] have studied the rate of reduction of pinene in various solvents. In formic acid and in alcohol hydrogenation proceeded very slowly, and the activity of the catalyst was observed to decrease. In ether the activity diminished in a similar manner, but no catalytic poisoning was noted. In ethyl acetate reduction took place regularly at first, then stopped, the activity of the catalyst being, however, not permanently impaired, a similar effect being observed in acetic acid. These hydrogenations were carried out at the ordinary temperature in a shaker.

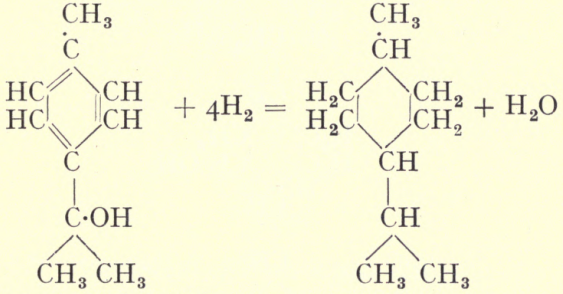
By distilling pulegone together with hydrogen over a nickel catalyst at an elevated temperature, Skita and Ritter[3] obtained menthane.

[1] Skita and Meyer, *Ber.*, 1912, **45**, 3579.
[2] Böeseken and Bilheimer, *Rec. trav. chim. Pays-Bas*, 1916, **35**, 288.
[3] Skita and Ritter, *Ber.*, 1912, **45**, 668.



Pulegone. Menthane.

Menthane has also been obtained by Smirnoff[1] in a similar manner from *p*-tolylisopropyl alcohol :

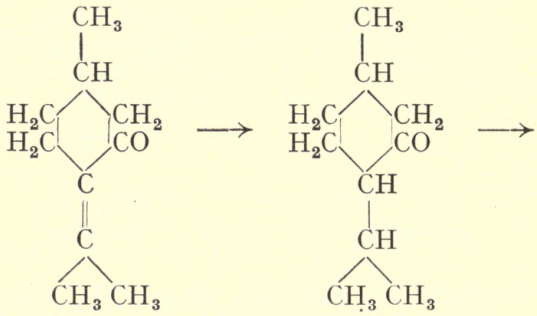


Tolyl isopropyl alcohol.

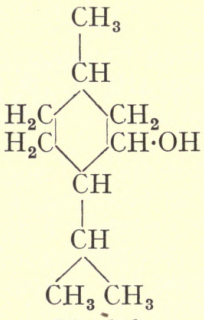
Working with hydrogen under a pressure of approximately 100 atmospheres in presence of a nickel catalyst, Ipatiew and Balatschinsky[2] observed that the formation of menthol and menthane from pulegone (by reduction of the CO group) only took place above 250° C. At lower temperatures,

[1] Smirnoff, *J. Russ. Chem. Phys. Soc.*, 1909, **41**, 1374.
[2] Ipatiew and Balatschinsky, *Ber.*, 1911, **44**, 3461.

hydrogen was added normally to the double bond, menthone being formed :



Pulegone. Menthone.

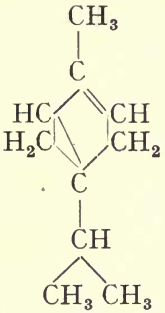


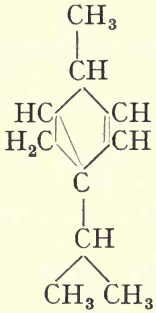
Menthol.

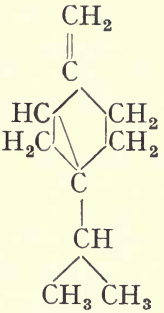
Analogous results were obtained with carvone and with thymol.

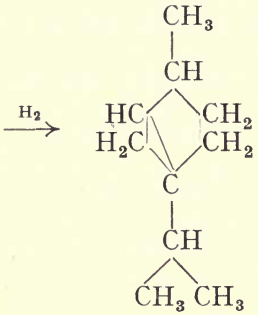
The hydrogenation of the thujenes and of sabinene has been effected by Tschugaeff and Fomin,[1] thujane being obtained in each case.

[1] Tschugaeff and Fomin, *Compt. rend.*, 1910, **151**, 1058.


α-Thujene.


β-Thujene.


Sabinene,


Thujane.

Hydrogenation of Heterocyclic Rings

Sabatier and Mailhe[1] attempted to hydrogenate pyridine by the vapour method, but were able to obtain only a splitting of the pyridine ring without direct hydrogenation of the unsaturated linkages contained therein. Pyridine is, however, easily reduced to piperidine by treatment with hydrogen at the ordinary temperature in acetic acid solution in the presence of colloidal platinum,[2] while quinoline was found to pass successively into the tetra- and

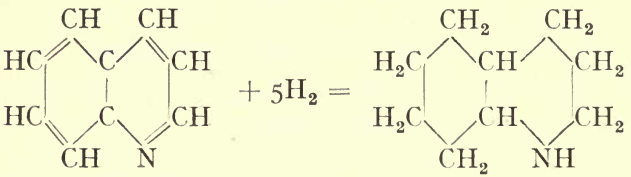
[1] Sabatier and Mailhe, *Compt. rend.*, 1907, **144**, 784.
[2] Skita and Meyer, *Ber.*, 1912, **45**, 3579.

decahydro reduction products, the pyridine nucleus being attacked before the benzene ring.

Skita and Brunner[1] have effected the reduction of pyridine to piperidine in dilute hydrochloric acid solution. Hydrogenation was also effected with *a*-picoline, of *aγ*-lutidine and of 2 : 4 : 5-collidine, and good results were obtained in acetic acid solution at 25–45° C. with an excess pressure of three atmospheres in presence of platinum.

aγ-Phenyl quinoline carboxylic acid was reduced to tetrahydro-phenyl quinoline carboxylic acid at two atmospheres pressure at 50–60° C., while the decahydro-compound was obtained with hydrogen at a pressure of ten atmospheres, employing a larger quantity of catalyst.

The reduction of quinoline has also been carried out by Ipatiew[2] in presence of nickel in the course of his work on hydrogenation at high temperatures and pressures. Twenty grams of quinoline together with 2 grams of nickel oxide were treated with hydrogen for twenty hours at 240° C. at a pressure of 100 atmospheres, complete transformation into decahydro-quinoline being obtained :

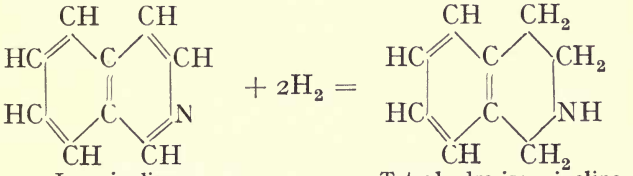


Quinoline.

Isoquinoline, on the other hand, has up to the present only been hydrogenated to the tetrahydro-derivative. It would seem, therefore, in this case at any rate, that the heterocyclic ring is more easily

[1] Skita and Brunner, *Ber.*, 1916, **49**, 1597.
[2] Ipatiew, *ibid.*, 1908, **41**, 991.

reduced catalytically than the benzene nucleus, this being the case also with nascent hydrogen.



Isoquinoline. Tetrahydro-isoquinoline.

The hydrogenation of pyrrol to pyrrolidine by the vapour method in presence of nickel has been carried out by Padoa.[1] In the case of indol, however, decomposition took place[2] with formation of toluidine. Decomposition is also found to attend the hydrogenation of acridine by Sabatier's method, the principal product of the reaction being *aβ*-dimethyl quinoline.

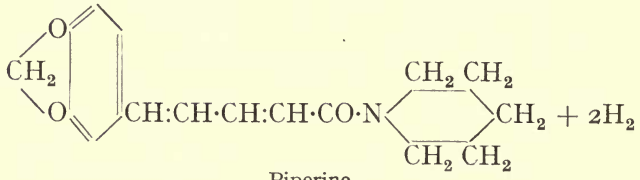
Of other heterocyclic rings, the hydrogenation of furfurane derivatives has also been studied, reduction proceeding normally.

Hydrogenation of Alkaloids and other Bodies possessing a Complicated Structure.

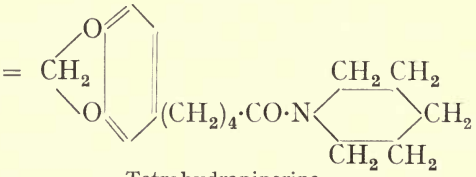
Catalytic hydrogenation has made easy the production of many derivatives of alkaloids, such derivatives often possessing valuable modifications of the properties of the parent substance. Thus, taking a few typical examples, quinine and cinchonine are easily hydrogenated to dihydroquinine and dihydrocinchonine in presence of palladium.[3] Cinchonidine,[4] tropine and dimethyl piperine[5] behave

[1] Padoa, *Att. Lincei*, 1906, **15**, I, 219.
[2] Padoa, *ibid.*, 1906, **15**, I, 699.
[3] Skita and Franck, *Ber.*, 1911, **44**, 2862.
[4] Skita and Franck, *ibid.*, 1912, **45**, 3312.
[5] Skita and Franck, *ibid.*, 1910, **43**, 1176.

similarly, while piperine[1] takes up four atoms of hydrogen, with saturation of its aliphatic chain, the benzene nucleus being left unattacked.



Piperine.



Tetrahydropiperine.

Morphine, on being treated with hydrogen in presence of palladium, is found to pass into dihydromorphine. Strychnine[2] is hydrogenated to a dihydrostrychnine, which is not identical with the dihydroderivative obtained by non-catalytic reduction of the base and, unlike this, is capable of being further hydrogenated to tetrahydrostrychnine. Morphine, brucine, and codeine also yield dihydro-products.

Of non-alkaloidal substances possessing a complicated structure, santonine has been hydrogenated to tetrahydrosantonine. Similarly, phytol and cholesterine have been reduced by Willstätter and Mayer[3] to dihydrophytol and dihydrocholesterine respectively, using a platinum catalyst in ethereal solution.

[1] Borsche, *Ber.*, 1912, **45**, 2943. Skita and Meyer, *ibid.*, 1912, **45**, 3579.

[2] Skita and Frank, *loc. cit.*

[3] Willstätter and Mayer, *Ber.*, 1908, **41**, 1475, 2199.

CHAPTER VI

Miscellaneous Reductions

We have up to the present considered principally cases of simple introduction of hydrogen into unsaturated linkages. There are, however, reactions in which something more than this occurs, and to these, together with the direct hydrogenation of various linkages other than those already treated, it is proposed to devote the present chapter.

Perhaps the simplest example of a reduction differing essentially in character from a simple saturation with hydrogen is to be found in the production of methane from carbon monoxide or carbon dioxide.

Sabatier and Senderens,[1] in 1902, found that, on passing a mixture of carbon monoxide and hydrogen over nickel, formation of methane began at 200° C. and took place easily and smoothly at 250° C. Similar results were obtained with mixtures of carbon dioxide and hydrogen, a suitable reaction temperature being in this case 300° C. Cobalt was found to be less active and to require a higher reaction temperature than nickel.

$$CO + 3H_2 = CH_4 + H_2O$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

A copper catalyst was found to be incapable of inducing the complete reduction of carbon dioxide to methane, carbon monoxide only being obtained.

$$CO_2 + H_2 = H_2O + CO.$$

[1] Sabatier and Senderens, *Compt. rend.*, 1902, **134**, 514, 689.

Vignon,[1] who studied the reduction of carbon monoxide to methane at a later date, recommends nickel as the most suitable catalyst and 600° C. as the optimum temperature.

Examples of the reduction of the carbonyl group of organic compounds to CH·OH or to CH_2 have already been given in the preceding chapters, usually in connection with the simultaneous saturation of an ethylenic, acetylenic, or benzenoid linkage. Some cases of reduction of a carbonyl group, unaccompanied by such saturation, will be considered here.

The action of hydrogen on acetone in presence of platinum has been investigated by Vavon.[2] In ethereal solution, reduction to propane was obtained, but the reaction was found soon to come to a standstill, probably by reason of the presence of poisons in the acetone used.

$$CH_3{\cdot}CO{\cdot}CH_3+2H_2 = H_2O+CH_3{\cdot}CH_2{\cdot}CH_3.$$

If, however, the acetone is diluted with an equal volume of water and hydrogenated in this condition in presence of platinum, a slow and complete reduction to isopropyl alcohol was observed.

$$CH_3{\cdot}CO{\cdot}CH_3+H_2 = CH_3{\cdot}CH{\cdot}OH{\cdot}CH_3.$$

Similarly, secondary butyl alcohol was obtained from diluted methyl ethyl ketone. Acetophenone in ether, alcohol, ethyl acetate, or acetic acid solution is converted to the corresponding hydrocarbon, while, on carrying out the reduction in dilute alcoholic solution, formation of almost pure phenyl-ethyl-carbinol takes place. It will be noticed that, in general, organic solvents lead to a complete reduction to hydrocarbon, while an aqueous solution of the body to be reduced is only converted to alcohol.

[1] Vignon, *Compt. rend.*, 1913, **157**, 131.
[2] Vavon, *ibid.*, 1912, **155**, 286.

The catalytic reduction of a CO group to CH_2 has been used by Borsche[1] for the preparation of $\omega\omega'$-diaryl aliphatic hydrocarbons. The first stage in the synthesis consists in a condensation of the following type :

$$\begin{matrix} CH_2\cdot COCl \\ | \\ CH_2\cdot COCl \end{matrix} + 2C_6H_6 = \begin{matrix} CH_2\cdot CO\cdot C_6H_6 \\ | \\ CH_2\cdot CO\cdot C_6H_6 \end{matrix} + 2HCl,$$

the resulting product being dissolved in methyl alcohol and hydrogenated at the ordinary temperature in presence of colloidal palladium.

$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot C_6H_5 + 4H_2 = C_6H_5\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot C_6H_5 + 2H_2O$$

By reducing the ketone,

$$C_6H_5\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2\cdot C_6H_5,$$

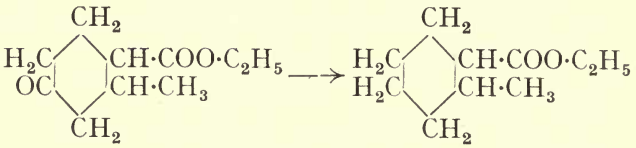
in presence of not very active nickel at 180° C., Sabatier and Murat [2] obtained $\omega\omega'$-diphenyl pentane, $C_6H_5\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot C_6H_5$, while similar treatment in presence of very active nickel at 165° C. gave the corresponding dicyclohexyl pentane, the benzene nucleus being, in this case, also attacked.

Various aliphatic diketones, on the other hand, were found by Sabatier and Mailhe [3] to be hydrogenated by distillation over nickel to corresponding alcoholic bodies.

The reduction of a carbonyl group to CH_2 in presence of nickel can also be effected when the carbon atom is a member of a ring. Thus Skita[3] hydrogenated, by distillation with hydrogen over

[1] Borsche, *Ber.*, 1911, **44**, 3185.
[2] Sabatier and Murat, *Compt. rend.*, 1913, **156**, 1951.
[3] Sabatier and Mailhe, *ibid.*, 1907, **144**,, 1086.
[4] Skita, *Ber.*, 1909, **42**, 1627.

nickel, the esters of the cyclohexanone carboxylic acids to esters of the naphthenic acids:



An exceedingly interesting method for the conversion of the CO group into CH_2 has been described by Ipatiew[1] for certain ketones of the terpene class. It consists in the combined action of a hydrogenating and of a dehydrating catalyst, the ketone being first reduced to a secondary alcohol under the influence of the hydrogenating catalyst present. The secondary alcohol, in presence of the dehydrating catalyst, passes by loss of water into an unsaturated hydrocarbon which, in its turn, takes up hydrogen to form a saturated hydrocarbon.

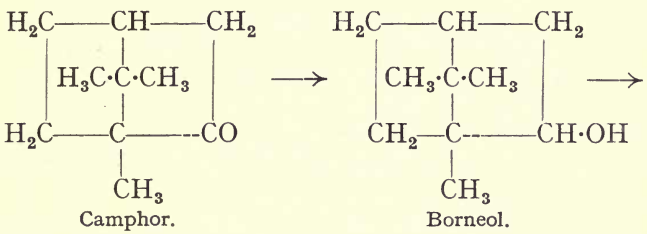
The series of reactions is found to take place at a much lower temperature when carried out simultaneously than when brought about by the separate action of the hydrogenation and dehydration catalysts. Thus, while the hydrogenation of camphor to borneol by means of nickel in Ipatiew's high pressure apparatus required a temperature of from 320° C. to 350° C., and the dehydration of borneol to camphene 350° C. to 360° C., the camphene being easily hydrogenated to camphane in presence of nickel at 240° C., the transformation of camphor to isocamphane in presence of a catalyst consisting of a mixture of nickel oxide and aluminium oxide takes place at 200° C., or even less.

Ipatiew found it impossible, even at 400° C., to obtain camphane from camphor by direct hydrogenation in presence of nickel oxide.

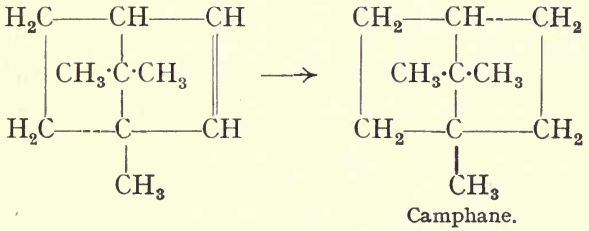
Another instance of the difference in the activity

[1] Ipatiew, *Ber.* 1912, **45**, 3205.

of nickel and copper may be observed by substituting copper for nickel in the above combined hydrogenation and dehydration catalyst. In this case the reaction stops at camphene, which, in the presence of copper, is not further reduced. Further, instead of starting with camphor, borneol or isoborneol may be taken. From either of these isocamphane can be obtained by the action of the combined catalyst in a pressure apparatus at 215° C.



Camphor. Borneol.



Camphane.

Similar results have been obtained for the hydrogenation of fenchone to fenchane in presence of nickel and alumina.

The reduction of the oxymethylene group, according to Paal's or Skita's method, has been studied by Kötz and Schaeffer.[1] From oxymethylene acetoacetic ester, methyl acetoacetic ester was obtained. Other oxymethylene compounds were found to be capable of being reduced similarly.

[1] Kötz and Schaeffer, *Ber.*, 1912, **45**, 1952.

Hydrogenation of the C:N *Group*

Sabatier and Senderens[1] succeeded in preparing various aliphatic amines by the catalytic reduction of nitriles by the vapour method over nickel at 180–200° C., a reduction which is also easily effected by nascent hydrogen. The primary amine formed, however, was found to pass, by loss of ammonia, to some degree into a secondary or tertiary amine :

$$CH_3{\cdot}C{:}N + 2H_2 = CH_3{\cdot}CH_2{\cdot}NH_2$$

$$2CH_3{\cdot}CH_2{\cdot}NH_2 = \begin{matrix} CH_3{\cdot}CH_2 \\ \\ CH_3{\cdot}CH_2 \end{matrix}\!\!\diagdown\!\!\diagup NH + NH_3$$

$$3CH_3{\cdot}CH_2{\cdot}NH_2 = (CH_3{\cdot}CH_2)_3N + 2NH_3$$

Aromatic nitriles, on being reduced in a similar way, gave as the principal reaction product a mixture of amines, hydrocarbons, and ammonia.

The reduction of the C:N group may also be carried out at the ordinary temperature in presence of colloidal platinum or palladium. Paal and Gerum[2] reduced in this way benzonitrile in alcoholic solution to a mixture of benzylamine, dibenzylamine, and ammonia, together with a little benzaldehyde.

Mandelic nitrile—the cyanhydrin of benzaldehyde—was converted by a similar hydrogenation to mono- and di-benzylamine, ammonia, and benzyl alcohol, decomposition taking place, while benzaldoxime was found to give the same reduction products as those obtained from benzonitrile. Similarly, acetonitrile is reduced in presence of colloidal palladium to ethylamine : [3]

$$\underset{\text{Benzonitrile.}}{C_6H_5{\cdot}CN} + 2H_2 = \underset{\text{Benzylamine.}}{C_6H_5{\cdot}CH_2{\cdot}NH_2}$$

$$\underset{\text{Benzaldoxime.}}{C_6H_5{\cdot}CH{:}NOH} + 2H_2 = C_6H_5{\cdot}CH_2{\cdot}NH_2 + H_2O.$$

[1] Sabatier and Senderens, *Compt. rend.*, 1905, **140**, 482.
[2] Paal and Gerum, *Ber.*, 1909, **42**, 1553.
[3] Skita, *Ber.*, 1909, **42**, 1636.

Reduction of Isonitriles.

Isonitriles, on being subjected to catalytic hydrogenation, give, in accordance with their constitution, a reaction product differing essentially from that obtained from the corresponding nitrile. Sabatier and Mailhe,[1] who studied the reduction of aliphatic carbylamines by distillation with hydrogen over nickel, obtained, in general, a reaction of the following type :

$$CH_3{\cdot}N{:}C + 2H_2 = CH_3{\cdot}NH{\cdot}CH_3.$$

It was found that a copper catalyst could be substituted for the nickel, but was less active.[2] The course of the reduction should be compared with that of the true nitriles described above.

Reduction of Isocyanic Esters.

Ethyl isocyanate, on being distilled with hydrogen over nickel at 250–290° C., was converted principally into secondary methyl-ethyl-amine.[3]

$$O{:}C{:}N{\cdot}C_2H_5 + 3H_2 = CH_3{\cdot}NH{\cdot}C_2H_5 + H_2O$$

Reduction of the –N:N– *Group.*

Skita [4] dissolved 9 grams of azobenzene in 250 c.c. of alcohol and added 35 c.c. of colloidal palladium solution, containing 0·03 gram of palladium and 0·05 gram of gum arabic. On hydrogenating in a shaker with hydrogen under an increased pressure of one atmosphere, the theoretical volume of hydrogen for production of hydrazobenzene was absorbed in five minutes, while, on continuing the

[1] Sabatier and Mailhe, *Compt. rend.*, 1907, **144**, 955.
[2] Sabatier and Mailhe, *Bull.*, 1907, **1**, 612.
[3] Sabatier and Mailhe, *Compt. rend.*, 1907, **144**, 824.
[4] Skita, *Ber.*, 1912, **45**, 3312.

treatment for $4\frac{1}{2}$ hours, the hydrazobenzene was completely reduced to aniline :

$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_5+H_2 = C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5$$
$$C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5+H_2 = 2C_6H_5{\cdot}NH_2.$$

It will be noticed that the reduction to hydrazobenzene takes place far more rapidly than the conversion of this to aniline.

Reduction of Oxides of Nitrogen.

Oxides of nitrogen are easily reduced to ammonia by treatment with hydrogen in presence of a suitable catalyst. Sabatier and Senderens[1] recommend nickel, but state that copper may also be used. A somewhat similar reaction has been noticed by the author in the course of the reduction by hydrogen of a mixture of pure iron and sodium nitrate at an elevated temperature. The reduction of nitrites to ammonia in presence of palladium is mentioned by Bredig.[2]

It is interesting in connection with reactions of the above type to note that the easy reduction of hydroxylamine to ammonia by hydrogen in presence of platinum was observed by Victor Meyer[3] as long ago as 1891.

Reduction of Nitro-compounds.

The catalytic reduction of nitrobenzene and nitromethane to aniline and methylamine by leading the vapours of these bodies together with hydrogen over palladium was, as already mentioned, noticed by Saytzeff in 1871.[4]

[1] Sabatier and Senderens, *Compt. rend.*, 1902, **135**, 278.
[2] Bredig, *Anorg. Fermente*,, Leipzig, 1904, p. 46.
[3] Victor Meyer, *A.*, 1891, **264**, 126.
[4] Kolbe and Saytzeff, *J. prakt. Chem.*, 1871, **4**, 418.

Sabatier and Senderens[1] recommend finely divided copper at 300–400° C. as the most suitable catalyst for the conversion of nitrobenzene to aniline, and state that if too little hydrogen be employed, azobenzene is formed.

$$C_6H_5{\cdot}NO_2+3H_2 = C_6H_5{\cdot}NH_2+2H_2O$$
$$2C_6H_5{\cdot}NO_2+4H_2 = C_6H_5{\cdot}N{:}N{\cdot}C_6H_5+4H_2O.$$

Nickel was found to be too energetic and to tend to split off ammonia with the formation of benzene or, at temperatures above 300° C., even of methane. Cobalt and iron behave similarly to nickel. Finely divided platinum at 230–300° C. induces a normal reduction to aniline, but if insufficient hydrogen for complete reduction be present, hydrazobenzene is formed.

$$2C_6H_5{\cdot}NO_2+5H_2 = C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5+4H_2O.$$

The reaction was extended in a later paper[2] to other nitro-compounds, including *α*- and *β*-nitronaphthalenes. Copper was again found to be more suitable than nickel, the action of which was too violent, and gave rise to ammonia and tetrahydronaphthalene.

Paal and Gerum[3] examined the reduction of nitrobenzene to aniline in presence of colloidal metallic catalysts at temperatures varying from 60–85° C. and in alcoholic solution. Colloidal palladium, prepared according to Paal and Amberger's method by the reduction with hydrazine hydrate of a palladium chloride solution containing sodium protalbinate as a protective colloid, was found to be an excellent catalyst for the reaction in question. Colloidal copper and gold were found to be inactive, colloidal silver and osmium slightly active. The reduction of nitrobenzene to aniline and of *o*-nitro-

[1] Sabatier and Senderens, *Compt. rend.* 1901, **133**, 321. See also Senderens, German patent 139457 (1901).
[2] Sabatier and Senderens, *ibid.*, 1902, **135**, 225.
[3] Paal and Gerum, *Ber.*, 1907, **40**, 2209.

acetophenone to *o*-aminoacetophenone has also been studied by Skita and Meyer.[1]

An interesting variation in the course of the catalytic reduction of nitro-compounds is described by Brochet.[2] Nitrobenzene in alkaline solution is found to pass through azoxybenzene, azobenzene, and, finally, hydrazobenzene before becoming converted to aniline. A similar reduction by nascent hydrogen in alkaline solution had, of course, long been known.

$$\underset{\text{Nitrobenzene.}}{2C_6H_5\cdot NO_2}+3H_2 = \underset{\text{Azoxybenzene.}}{C_6H_5\cdot N(O)N\cdot C_6H_5}+3H_2O$$

$$C_6H_5\cdot N(O)N\cdot C_6H_5+H_2 = \underset{\text{Azobenzene.}}{C_6H_5\cdot N{:}N\cdot C_6H_5}+H_2O$$

$$C_6H_5\cdot N{:}N\cdot C_6H_5+H_2 = \underset{\text{Hydrazobenzene.}}{C_6H_5\cdot NH\cdot NH\cdot C_6H_5}$$

$$C_6H_5\cdot NH\cdot NH\cdot C_6H_5+H_2 = \underset{\text{Aniline.}}{2C_6H_5\cdot NH_2}$$

Paal and Hartmann[3] take advantage of the ease of reduction of nitro-groups in devising a method for the volumetric estimation of hydrogen in gas mixtures. These authors point out the advantages accruing from the employment of a liquid absorbing medium instead of the solid palladinised asbestos usually employed, in that dead space may be eliminated by using a Hempel absorption pipette either of the usual type or of the slightly modified form described in Paal and Hartmann's paper.

[1] Skita and Meyer, *Ber.*, 1912, **45**, 3579.
[2] Brochet, first addition, dated Oct. 8, 1912, to French patent 458033.
[3] Paal and Hartmann, *Ber.*, 1910, **43**, 243.

An effective absorbing liquid is prepared by dissolving 5 grams of sodium picrate and 2·5 grams of colloidal palladium in 200 c.c. of water. During an analysis, the pipette is shaken from time to time. Absorption should be complete after about ten minutes.

Removal of Halogens by Hydrogen.

C. Kelber[1] has proposed to utilise the catalytic removal of halogens from organic compounds by hydrogen in presence of nickel or palladium as an analytical method for the quantitative estimation of halogens. The catalysts recommended are either palladinised calcium carbonate or nickel reduced from carbonate at 310–320° C. For a determination, three grams of the catalyst are placed in a reaction vessel attached to a shaker and shaken with water or dilute alcohol in presence of hydrogen until no more of the gas is absorbed. The substance to be analysed is now added and shaking continued until hydrogen absorption ceases, when the catalyst is filtered off and the halogen in the filtrate determined gravimetrically or by titration.

Catalytic Reduction of Metallic Oxides.

The direct reduction to metal of nickel and copper oxides is a remarkable example of the activation of hydrogen by means of catalysts. Paal,[2] working in this direction, has found that freshly precipitated, or colloidal, copper or nickel hydroxide can be reduced to colloidal metals by treatment with hydrogen at the ordinary temperature in presence of colloidal palladium.

[1] Kelber, *Ber.*, 1917, **50**, 305.
[2] Paal, *ibid.*, 1914, **47**, 2202.

Paal and Büttner[1] have investigated further the reduction of ammonium molybdate in presence of colloidal palladium. At the ordinary temperature reduction took place slowly and stopped at the tetrahydroxide. On raising the temperature to 60° C. reduction recommenced, black molybdenum trihydroxide being precipitated.

[1] Paal and Büttner, *Ber.*, 1915, **48**, 220.

CHAPTER VII

Dehydrogenation

The simple dehydrogenation of straight carbon–hydrogen chains has up to the present not been realised. Ipatiew showed, however, that alcohol could be dehydrogenated to aldehyde in presence of finely divided copper,

$$CH_3 \cdot CH_2 \cdot OH = CH_3 \cdot CHO + H_2.$$

Sabatier and Senderens[1] recommend leading alcohol over a copper catalyst at a temperature between 200° C. and 230° C. No formation of water or ethylene was noted under these conditions. Nickel and platinum appear not to be as suitable as copper for the promotion of the dehydrogenation and tend to lead to side reactions.

In a later paper, Sabatier and Senderens[2] describe the application of the reaction to other alcohols of the methane series. It is found, in general, that the lower the molecular weight of the alcohol, the easier is the dehydrogenation.

Unsaturated alcohols behave similarly, but are, as would be expected, liable to be hydrogenated simultaneously to saturated bodies. Allyl alcohol,[3] for instance, on being led over finely divided copper at 180–300° C., is dehydrogenated to acrolein, which

[1] Sabatier and Senderens, *Compt. rend.*, 1903, **136**, 738.
[2] Sabatier and Senderens, *ibid.*, 1903, 921.
[3] Sabatier and Senderens, *ibid.*, 1903, 983.

in turn combines to a certain degree with the hydrogen liberated, propyl aldehyde being formed:

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH = CH_2{:}CH{\cdot}CHO + H_2$$
$$CH_2{:}CH{\cdot}CHO + H_2 = CH_3{\cdot}CH_2{\cdot}CHO.$$

Similarly, benzyl alcohol, led over copper at 300° C., is dehydrogenated to benzaldehyde,

$$C_6H_5{\cdot}CH_2{\cdot}OH = C_6H_5{\cdot}CHO + H_2.$$

The dehydrogenation of alcohols in presence of copper affords an interesting test as to their nature. Primary alcohols decompose, as already described, according to the general equation

$$R{\cdot}CH_2{\cdot}OH = R{\cdot}CHO + H_2.$$

Secondary alcohols, on the other hand, pass by loss of hydrogen into ketones, while with tertiary alcohols unsaturated hydrocarbons are formed by dehydration instead of dehydrogenation:

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH{\cdot}OH = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CO + H_2$$

$$\begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix}\!\!>\!C{\cdot}OH = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{:}CH_2 + H_2O.$$

Sabatier and Gaudion[1] find that dehydrogenation of amines to nitriles may be effected either in presence of nickel at 300–350° C. or of copper at 300–400° C., according to the general equation

$$R{\cdot}CH_2{\cdot}NH_2 = R{\cdot}CN + 2H_2$$

The hydrogen is not, however, obtained to any degree as such, since it enters into side reactions with the original amine, with formation of ammonia. In the case of benzylamine, a yield of benzonitrile approximating to 30 per cent. was isolated, the

[1] Sabatier and Gaudion, *Compt. rend.*, 1917, **165**, 224.

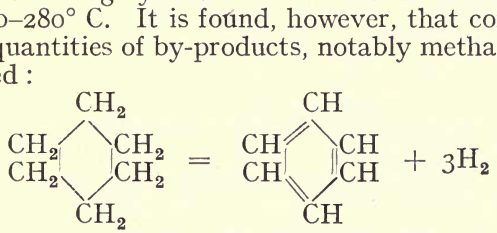
principal by-products being ammonia and toluene. Similarly, isoamylamine was converted into iso-valeronitrile.

$$\underset{\text{Isoamylamine.}}{(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2} = \underset{\text{Isovaleronitrile.}}{(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}CN} + 2H_2$$

The dehydrogenation of methyl alcohol to formaldehyde in presence of copper has been proposed by Mannich and Geilmann[1] as a method of detecting this body. The liquid under examination is passed over coppered pumice at 280–300°, the formaldehyde being recognised by the violet coloration which it produces with morphine and concentrated sulphuric acid.

Dehydrogenation of Reduced Benzene Derivatives.

The dehydrogenation of cyclohexane to benzene in presence of nickel was observed by Sabatier and Senderens[2] in 1901. Sabatier and Mailhe,[3] who subjected the reaction to a thorough study, recommend distilling cyclohexane over the nickel catalyst at 270–280° C. It is found, however, that considerable quantities of by-products, notably methane, are formed :



A more satisfactory reaction with absence of by-products is obtained by substituting palladium for nickel.[4] With this catalyst dehydrogenation begins at 170° C., is rapid at 200° C., and reaches its maxi-

[1] Mannich and Geilmann, *Arch. Pharm.*, 1916, **254**, 50.
[2] Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 566.
[3] Sabatier and Mailhe, *ibid.*, 1903, **137**, 240.
[4] Zelinsky, *Ber.*, 1911, **44**, 3121.

mum velocity at 300° C. Hexahydrotoluene behaves similarly. In a typical experiment, 22·3 grams of hexahydrobenzene were led over 16·6 grams of palladium black contained in a tube 38 cm. long and 14 mm. internal diameter. The complete distillation was carried out in twelve minutes at 300° C., 15·97 litres of hydrogen (83·5 per cent. of the theoretical volume) being produced. No tetra- or di-hydrobenzene was observed in the product. Platinum was found to be less active than palladium, while copper was inactive even at 300° C. The reaction is confined to hexa-rings, hexane or penta-rings, for instance, remaining unchanged after similar treatment.

A simultaneous dehydrogenation and hydrogenation has been observed in the case of tetrahydronaphthalene, the reaction product consisting of a mixture of naphthalene itself and of hydrogenated naphthalenes formed by the action of the hydrogen liberated by the dehydrogenation.

Passing from the dehydrogenation of cyclic hydrocarbons to that of their derivatives, the dehydrogenation of dihydroterephthalic acid may be mentioned. Knoevenagel[1] found, in 1903, that dehydrogenation of this body took place in presence of palladium, and obtained similar results with benzhydrol and benzoin.

The whole subject of dehydrogenation is one which has, up to the present, only been studied for isolated cases. Systematic investigation of the phenomenon would without doubt lead to the discovery of many more reactions in which bodies are capable of passing in presence of a suitable catalyst into a less hydrogenated substance and free hydrogen.

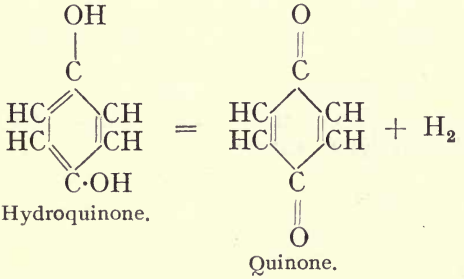
Several interesting examples of dehydrogenation at the ordinary temperature have been studied by H. Wieland,[2] who bases his experiments on the

[1] Knoevenagel, *Ber.*, 1903, **36**, 2816.
[2] H. Wieland, *ibid.*, 1911, **45**, 484.

view that, at any rate in many cases, hydrogenation of an unsaturated compound with an equivalent quantity of hydrogen would not proceed to completion, but would stop at a certain equilibrium, which could be displaced towards complete hydrogenation by a high concentration of hydrogen, this being the procedure usually adopted in actual hydrogenation practice.

If, however, such an equilibrium really exists, then it should be attainable also by starting with the hydrogenated substance.

In the investigation of the dehydrogenation of various bodies at the ordinary temperature, Wieland made use of specially prepared oxygen-free palladium in order to avoid the possibility of catalytic oxidation being mistaken for dehydrogenation. An aqueous solution of hydroquinone was found to be partially dehydrogenated to quinone by shaking with palladium black. The amount of quinone formed can be increased by raising the concentration of the hydrogen absorber—in this case the palladium. The metal here, besides acting as a catalyst, has also a non-catalytic, purely absorbent, function.



Hydroquinone. Quinone.

The dehydrogenation of hydrazobenzene and of dihydronaphthalene takes place much more completely than that of hydroquinone. The colourless solution of hydrazobenzene, on being shaken with palladium, immediately becomes yellow, and after

a few hours no trace of the original substance remains. The solution now contains azobenzene, aniline, and hydrogen absorbed by the palladium. This reaction is therefore another example of simultaneous dehydrogenation and hydrogenation, and is similar to those already mentioned.

$$C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5 = C_6H_5{\cdot}N{:}N{\cdot}C_6H_5 + H_2.$$

The hydrogen liberated then acts on unchanged hydrazobenzene according to the equation

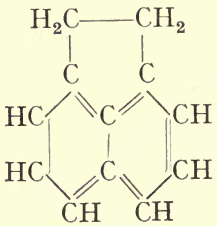
$$C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5 + H_2 = 2C_6H_5{\cdot}NH_2.$$

The dehydrogenation of dihydronaphthalene takes place in a similar way. Either alone or in benzene solution, it is converted into naphthalene and hydrogen, this latter acting on unchanged dihydronaphthalene to form tetrahydronaphthalene, which is found in the solution together with the naphthalene :

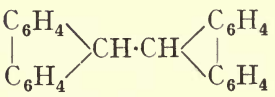
$$C_{10}H_{10} = C_{10}H_8 + H_2$$
$$C_{10}H_{10} + H_2 = C_{10}H_{12}.$$

Dihydroanthracene can also be dehydrogenated to anthracene, but the velocity of the reaction is much lower.

Wieland attempted in a similar way to dehydrogenate two bodies of the ethane type, acenaphthene and bidiphenylene ethane.



Acenaphthene.



Bidiphenylene ethane.

Only a trace of dehydrogenation was obtained under his conditions.

In a consideration of the mechanism of the dehydrogenation process, Wieland puts forward evidence for the intermediate formation of a compound between palladium and the saturated substance, this addition compound breaking up into palladium, hydrogen, and unsaturated body. He finds, on examining the dehydrogenation of alcohols to aldehydes by palladium black, that on adding palladium to alcohol a considerable evolution of heat takes place and a palladium is obtained from which the alcohol cannot be removed by a vacuum. On shaking the alcohol with the palladium for some time, aldehyde may be recognised in the solution. Ethyl alcohol undergoes dehydrogenation more rapidly than methyl alcohol, and higher alcohols still more so.

Wieland has put forward arguments for regarding certain oxidation reactions as being in reality cases of the dehydrogenation of the hydrate of the body in question. He has shown, for instance, that carbon monoxide, in presence of palladium and water, may be oxidised to carbon dioxide in complete absence of air or oxygen,[1] and suggests that the reaction takes place, not according to the ordinarily accepted formula, $2CO + O_2 = 2CO_2$, but according to the dehydrogenation equation,

$$CO + H_2O = CO_2 + H_2.$$

The hydrogen given off is absorbed by the palladium, or it may be removed by burning in air, as was done in Baumann and Traube's work on the same subject. The above equation says little about the course of the reaction. Wieland, however, was able to show that, as the first product of the action of water on carbon monoxide in presence of palladium, formic

[1] Wieland, *Ber.*, 1912, **45**, 679.

acid was formed, which decomposes in presence of the finely divided palladium into hydrogen and carbon monoxide, the hydrogen being absorbed by the palladium.

The course of the catalytic formation of carbon dioxide from carbon monoxide may therefore be represented thus :

$$CO + H_2O = \begin{matrix} H \\ OH \end{matrix}\!\!\rangle C{:}O$$

$$\begin{matrix} H \\ HO \end{matrix}\!\!\rangle C{:}O = CO_2 + H_2.$$

Wieland has further been able to recognise formic acid as the first product of the burning of carbon monoxide at high temperatures without a catalyst, by allowing a carbon monoxide flame to play on ice, and there seems no reason why the formation of carbon dioxide from carbon monoxide at all temperatures with or without a catalyst should not proceed by way of the same equation.

At a higher temperature, the reaction between carbon monoxide and water can be reversed, water and carbon monoxide being formed from carbon dioxide and palladium–hydrogen. Wieland regards the hydrogen peroxide found by Traube in the carbon monoxide as being produced by the burning of the hydrogen and oxygen.

In the same way, the oxidation of sulphur dioxide to sulphur trioxide is a reaction which does not proceed in absence of water, but can actually take place in the absence of oxygen, a phenomenon which may be explained by the dehydrogenation of sulphurous acid.[1] Wieland found that on leading moist oxygen-free sulphur dioxide over oxygen-free palladium black a considerable quantity of

[1] Wieland, *Ber.*, 1912, **45**, 685.

sulphuric acid was produced according to the equation

$$(1)\quad SO_2+H_2O = H_2SO_3$$

$$(2)\quad O_2S\begin{matrix}H\\ \diagdown\\ \diagup\\ OH\end{matrix} = SO_3+H_2.$$

Accordingly, the course of the reaction in the sulphuric acid contact process is not one of real oxidation, but a dehydrogenation in which the hydrogen split off by the platinum is taken up by the oxygen, while the water present in the system acts as a second catalyst, in a similar manner to the nitrous acid in the lead-chamber process. Wieland's results throw quite a new light on the necessity for, and *rôle* of, water in oxidation reactions generally.

CHAPTER VIII

The Technical Hydrogenation of Unsaturated Oils

The operation of "oil hardening," now carried out on an extensive scale for the manufacture of solid fats for use in the soap, edible fat, and candle industries, consists in the saturation with hydrogen of the glycerides of various unsaturated fatty acids, most of which contain a straight chain of eighteen carbon atoms and are thus convertible to stearic acid.

The following table summarises the most important acids of this class :

Acid.	Formula.	Contained in
Oleic acid	$CH_3(CH_2)_7 \cdot CH{:}CH \cdot (CH_2)_7 \cdot COOH$	Almost pure in olive oil.
Linolic acid	$CH_3(CH_2)_4 \cdot CH{:}CH \cdot CH_2 \cdot CH{:}CH(CH_2)_7 \cdot COOH$	Poppy oil, etc.
Linolenic acid	$C_{17}H_{29} \cdot COOH$	Linseed oil.
Clupanodonic acid	$C_{17}H_{27} \cdot COOH$	Fish oils.
Ricinoleic acid	$CH_3 \cdot (CH_2)_5 \cdot CH \cdot OH \cdot CH_2 \cdot CH{:}CH(CH_2)_7 \cdot COOH$	Castor oil.

The structure of the natural oils is complicated, not only by the variety of the acids present, but also

by reason of the tribasic character of glycerine, whereby the existence of various mixed glycerides becomes possible and, further, by the possibility of stereo-(*cis-trans*)isomerism.

The oils usually taken for hardening purposes are, *inter alia*, whale and other fish oils, cotton-seed oil, linseed oil, arachis oil, olive oil, rape oil, sesame oil, and castor oil.

In most cases the crude oil is found to contain various catalytically injurious impurities which must be removed before subjecting the material to hydrogenation. The exact method of refining will depend on the nature of the oil, but in general it may be stated that the object of the refining process should be to remove before everything free fatty acids, albuminous impurities, and traces of suspended water. For a detailed description of the methods, reference should be made to a work on oil refining, it being remembered that while almost any oil which is pure enough for edible purposes will harden satisfactorily, it is often unnecessary to refine to this degree.

The manufacture of the nickel catalyst on a large scale consists of a suitable modification of the methods described in Chapter II. In many works the nickel is employed on a porous support such as kieselguhr or pumice, it being either precipitated as hydroxide or carbonate on this supporting material, or the porous support may be immersed in a concentrated aqueous solution of nickel nitrate or in the salt melted in its water of crystallisation, the nitrate being in this case subsequently converted to oxide by ignition in the usual way. In any case, the dry carbonate or oxide thus obtained is reduced to nickel before use by means of a current of hydrogen, or the oxide may, if desired, be introduced in an unreduced condition into the oil and reduced there in conjunction with the hardening of the oil, in which case, however, the hydrogenation reaction is

necessarily carried out at a temperature higher than the reduction temperature of nickel oxide, for instance at 260° C., while hardening in presence of metallic nickel proceeds satisfactorily even at 160° C.

The activity of the catalyst and its power of resistance to the action of poisons may be modified to a very great degree by variations in the method of its preparation and reduction, as well as in the procedure adopted in the actual hydrogenation operation itself; further, the optimum catalyst for a particular sort of oil is, by reason of the impurities contained in the oil, not necessarily that which possesses the highest activity for the saturation of, for instance, pure oleic acid.

For the reduction of the nickel oxide in a dry condition various forms of plant have been described. The reducing gas employed is usually pure hydrogen, which is led over the oxide at a temperature of 300–350° C. The material after reduction should not, on account of the easily oxidisable and even pyrophoric nature of nickel reduced at low temperatures, be allowed, even when cold, to come into contact with air before immersion in oil. The reduction to metal is never complete, at any rate at temperatures suitable for the preparation of active nickel catalyst, and is facilitated by not exposing the oxide before reduction to a higher temperature than is necessary. Thus Sabatier and Espil state that nickel oxide prepared from nitrate by ignition at 550° C. was reduced to the extent of 93 per cent. by three hours' treatment with hydrogen at 240° C., while oxide prepared by ignition of nitrate at 800° C. was only reduced about 33 per cent. by a similar treatment.

A simple and efficient plant for the reduction of catalyst on a large scale is illustrated in Fig. 8.[1]

A horizontal cylindrical reduction vessel, along

[1] Ellis, "Hydrogenation of Oils," p. 192.

which the nickel is conveyed as required by means of special conveyors, may also be employed.

For the manufacture of catalyst for large installations several reduction units, of whatever type of continuously working reducer is adopted, may be connected together in series in such a way that that unit containing fresh oxide receives hydrogen which has already passed through the rest of the system,

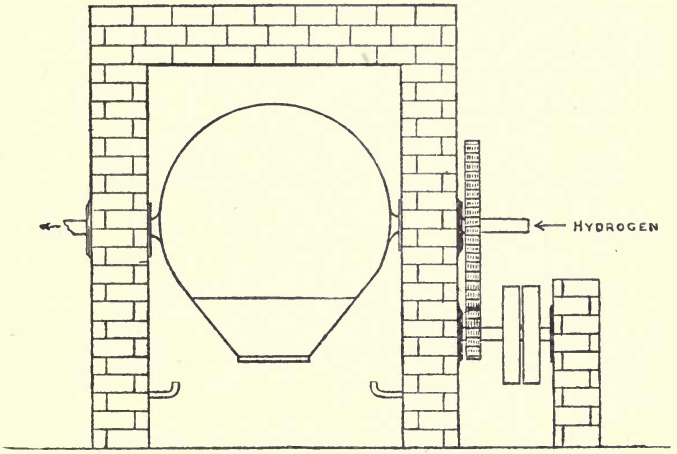


FIG. 8.

while fresh hydrogen enters at the unit containing nearly reduced nickel, or the nickel oxide itself may be moved through a sufficiently long heated system in counter-current to hydrogen, a continuous supply of reduced catalyst being in this way obtained. In designing a reduction apparatus suitable for continuous running it is, however, to be remembered that considerable quantities of reaction water are given off, accompanied by fine dust from the o ide, and that for this reason, unless straight exit tubes of sufficient diameter are provided, there is a

risk of these becoming choked by the mud thus formed.

If the nickel oxide is reduced in a dry condition the subsequent hardening operation may be carried out at 140–180° C. Should, however, the oxide be introduced as such into the oil it will be necessary, as already mentioned, in order to effect reduction, to heat this to 250° C. at least, an operation which with certain oils is undesirable in that it may, especially with oils containing highly unsaturated acids, lead to polymerisation and to the formation of undesirable decomposition products.

In addition to carefully prepared oil and catalyst, the use of hydrogen of as high a purity as possible and above all free from catalyst poisons is a factor of supreme importance in determining the speed and success of the hydrogenation reaction. For this reason, electrolytic hydrogen is, for purposes where the comparatively high cost of this is not prohibitive, a very suitable gas for catalytic reduction generally.

In view, however, of the high cost of electrolytic hydrogen, the production of pure hydrogen from water gas has in the last few years received considerable attention.

The most important methods of manufacturing hydrogen in this way are :—

(1) By the interaction of water gas and steam in presence of a catalyst.
(2) By the alternate reduction of iron oxide by water gas and oxidation of the iron with steam.
(3) By the low temperature separation of hydrogen from water gas.

For the manufacture of hydrogen by the first method, advantage is taken of the reaction between carbon monoxide and steam at elevated temperatures, whereby the carbon monoxide is oxidised to dioxide at the expense of the steam, with liberation

of an equivalent volume of hydrogen, according to the equation

$$CO+H_2O = CO_2+H_2,$$

the carbon dioxide being subsequently absorbed by compressing on to water or by other means. In order to displace the equilibrium as far as possible in the required direction it is essential first to carry out the reaction at as low a temperature as possible, in presence of an active catalyst, and secondly, as will be seen from the nature of the equation, to employ a large excess of steam. The equilibrium between carbon monoxide and steam has been studied by Hahn[1] (although for temperatures somewhat higher than those employed for the manufacture of hydrogen), but it is found difficult in practice to obtain by this method hydrogen free from carbon monoxide without subsequent purification with calcium carbide or with alkalies at an elevated temperature and pressure.

The reaction is carried out in practice by leading the mixture of water gas and steam through retorts containing a catalyst and maintained at 500–600° C., either by external heating or, according to a variation introduced by the Badische Anilin- & Soda-Fabrik[2] by injecting air or oxygen into the retorts together with the steam and water gas.

As a catalyst, iron is usually employed. Nickel and cobalt[3] have also been proposed, but have been found to be less efficient. The iron employed may be activated by the addition of promoters such as copper,[4] the alkalies,[5] preferably fixed to the iron as "ferrites" by previous ignition at a high temperature and subsequent lixiviation, or according

[1] Hahn, *Zeit. physikal. Chem.*, 1903, **42**, 705; **44**, 51; 1904, **48**, 735.
[2] Badische Anilin- & Soda-Fabrik, English patent, 27117/12.
[3] Mond and Langer, English patent, 12608/88.
[4] Buchanan and Maxted, English patent, 6477/14.
[5] Buchanan and Maxted, English patent, 6476/14.

to the Griesheim process[1] a contact mass containing lime, with or without iron, may be employed. In this case, the base has an absorbent function in addition to a catalytic one, part of the carbon dioxide produced being fixed as calcium carbonate,

$$CO+H_2O+CaO = CaCO_3+H_2.$$

The second method used for the manufacture of hydrogen consists in the alternate and separate treatment of iron oxide with an industrial reducing gas such as water gas and steam respectively. The process is by no means a recent one, and for details of earlier proposals reference may be made to the patent specifications, *inter alia*, of Hart,[2] Lewes,[3] and Lane.[4] In its modern form the plant is made in two types, consisting either of externally heated and usually vertical retorts or of internally heated producers, the heat in this case being applied by injection of air during the reducing phase. The material with which the retorts are filled may consist of natural iron ore, of compact iron, or of artificially prepared briquettes. Further, the yield for a given size of furnace may be increased by the incorporation or addition of promoters such as the oxides of lead, copper, chromium, or manganese.[5]

Hydrogen produced from water gas by the intermittent process contains as a rule, in addition to impurities capable of being removed by purifiers, from 1 to 3 per cent. of carbon monoxide. This impurity is not, as in hydrogen manufactured by the continuous process, a direct residue from the water gas used for reduction, but is formed by the action of steam on carbon deposited on the iron contact mass during the reducing phase by decom-

[1] Griesheim Elektron, English patent, 2523/09.
[2] Hart, English patent, 7741/89.
[3] Lewes, English patent, 20752/90 and 4134/9.
[4] Lane, English patent, 10356/03.
[5] Jaubert, English patent, 22126/10; Messerschmitt, French patent, 461480 (1913); Saubermann, English patent, 401/11.

position of carbon monoxide contained in the water gas used for such reduction.

Carbon monoxide, especially at temperatures below 200° C., exerts an injurious effect on the hardening of oils,[1] and in order to obtain a maximum speed of reaction, at any rate under the usual industrial conditions, it is therefore necessary to employ hydrogen free from this impurity.

This absence of carbon monoxide may be obtained by modifying the ordinary intermittent process in such a way that no carbon is deposited during the reducing phase. The deposition takes place by reason of the fact that carbon monoxide at high temperatures, especially in the presence of a catalyst such as iron, is unstable, passing into a mixture of carbon dioxide, carbon, and unchanged monoxide according to the equation,

$$2CO = CO_2 + C.$$

The carbon thus produced persists into the steaming phase, where, by the action of steam, carbon monoxide is generated simultaneously with the production of hydrogen by the interaction of the steam with the reduced iron. Such deposition of carbon may be prevented by employing for the reduction a special reducing gas containing a sufficient proportion of carbon dioxide to monoxide to approximate to or exceed the carbon dioxide–carbon monoxide equilibrium ratio for the temperature and conditions used for reduction,[2] such reducing gas being employed without the introduction into the retorts of air or steam during the reducing phase, or, if desired, air[3] or steam[4] may be introduced into the retorts during the reduction phase in addition to ordinary water gas.

[1] Caro, *Seifensieder Zeitung*, 1913, 852.
[2] Maxted and Ridsdale, English patent, 12896/15.
[3] Messerschmitt, English patent, 17691/13.
[4] Dellwik Fleischer Wassergas Ges., English patent, 21479/08.

Working with the first of these methods, the author has obtained a gas containing not the slightest trace of carbon monoxide and possessing the following composition :

Hydrogen	99·94
Carbon monoxide	nil.
Carbon dioxide	,,
Nitrogen	0·06
	100·00

For the attainment of this high degree of freedom from traces of air or its components, it is necessary to employ heated feed-water for the boiler generating steam for the hydrogen plant, and to instal surface condensers in preference to open water scrubbers.

The freedom of hydrogen from traces of carbon monoxide may also be effected by purifying the impure gas by compression on to alkalies with formation of formates,[1] or by treatment with heated calcium carbide according to Frank's method. Using an 80 per cent. soda solution for the purification, a pressure of 50 atmospheres at 260° C. is employed, so that while the method is extremely suitable for the synthesis of ammonia, it is in general preferable for catalytic hydrogenation to prepare the hydrogen directly in a pure condition without having recourse to a subsequent rather difficult purification process.

Passing to the third general method of hydrogen manufacture, namely, the low temperature separation of the constituents of water gas (hydrogen and carbon monoxide), it will be seen that the maximum purity of the hydrogen obtainable will under normal conditions be determined by the partial pressure of carbon monoxide at the lowest temperature employed in the separation.

[1] Badische Anilin- & Soda-Fabrik, English patent, 1759/12.

The vapour pressure of carbon monoxide at various temperatures is given in the following table :[1]

Temperature.	Vapour pressure of CO.
−183° C.	1722 mm.
−188	1065
−193	616
−198	329
−203	158
−205	114
−207	Solidification point.

Since it is desirable in low temperature separations to avoid the deposition of solid bodies, which by obstruction, especially in tubular exchangers, may seriously endanger the smoothness and continuity of running, it will be seen that the low temperature method, even if carried out at temperatures approaching the solidifying point of carbon monoxide, will not give by itself hydrogen of sufficient purity for catalytic use. The purity may be increased by working at an elevated pressure, but it is found necessary to separate the last traces of carbon monoxide by treatment with calcium carbide according to Frank's method, or by compression on to heated alkalies or alkaline earths with formation of formates as already described.

For details of the plant utilised in the commercial manufacture of hydrogen by this method, reference is made to the original patent specifications of Linde and others.[2]

For the carrying out of the fat-hardening reaction itself, various forms of plant have been devised, the effect desired being to obtain as intimate a contact as possible between the gaseous, liquid, and solid phases of the system, represented by hydrogen, oil, and nickel respectively.

[1] Baly and Donnan, *Trans. Chem. Soc.* 1902, **81**, 919.

[2] Linde, English patents, 7205, 1911 ; 9260, 1911. Frank, English patent, 26928, 1906, Société L'Air Liquide, English patents, 7147, 1913 ; 13160, 1914.

The degree of contact obtained by the simple bubbling of hydrogen through a vessel containing heated oil and nickel is insufficient for the satisfactory carrying out of the hydrogenation in practice, where a high reaction velocity and consequent large output for a plant of given size are essential for economic success.

A well-known design of plant in which this contact is increased by spray action is that evolved by

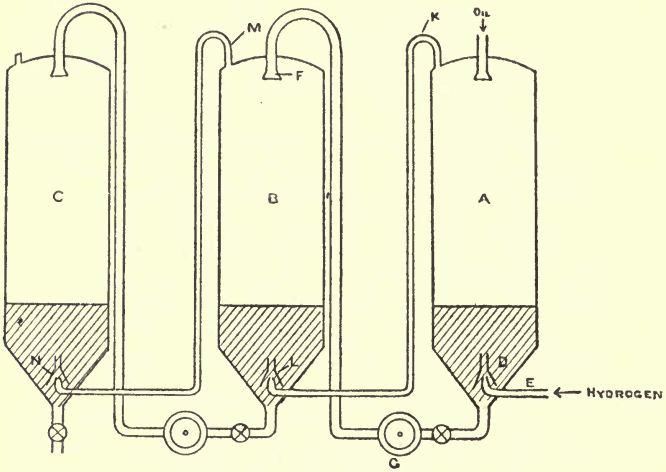


FIG. 9.

Wilbuschewitsch.[1] It consists of a series of autoclaves connected together in such a way (see Fig. 9) that hydrogen and oil containing finely divided nickel are passed in counter-current to one another through each unit of the system by means of sprays as shown. The oil is introduced at the top of the first autoclave, *A*, and, collecting in the conical reservoir, *D*, at the bottom, is partly projected into the hydrogen

[1] Wilbuschewitsch, English patent, 30014/10.

atmosphere by means of the gas entering the vessel at *E* and partly conveyed to the spray, *F*, at the top of the next vessel by means of the pump, *G*, the oil subsequently passing in a similar manner from *B* to *C*. The hydrogen, entering the vessel *A* by way of the jet, *E*, passes through the system by means of *K*, *L*, *M*, and *N*. The pressure employed is about nine atmospheres, a suitable initial temperature being 150–160° C.

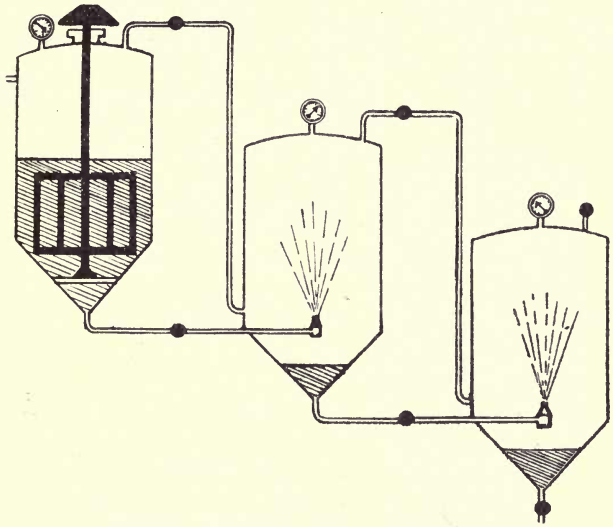


FIG. 10.

Testrup[1] projects the mixture of oil and catalyst by means of hydrogen pressure from vessel to vessel of a series of autoclaves somewhat similar to that employed by Wilbuschewitsch, the pressure being allowed to decrease from vessel to vessel in order to obtain the spraying effect desired (see Fig. 10).

[1] Testrup, English patent, 7726/10.

A plant which is capable of bringing about intimate contact between oil and hydrogen without the use of several vessels is illustrated in Fig. 11.[1] The oil alone is circulated by means of the rotary pump, *A*, and, entering the vessel by the jet *B*, causes by injector action in *C* the mixing effect necessary for the shortening of the time of reaction.

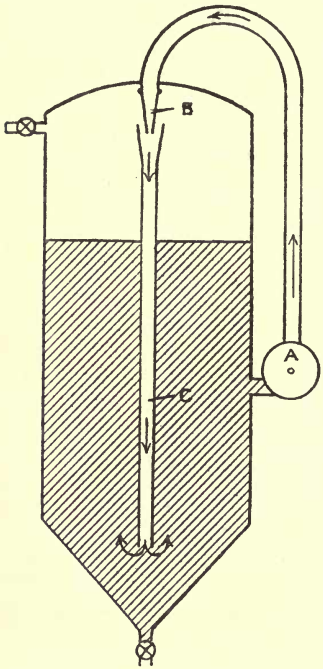


FIG. 11.

Calvert[2] mixes the oil and gas by means of a rotary stirrer driven by an electric motor contained in an extension of the autoclave and under a hydrogen pressure equal to that at which the reaction is carried out.

The author[3] has employed a plant in which an intimate mixing of practically the whole of the oil under treatment with hydrogen is obtained by projecting the oil and hydrogen in counter-current to one another through a column provided with a series of fixed propeller-like baffles, by the action of which the moving oil-gas mixture is alternately rotated clockwise and anti-clockwise respectively, the circulation being carried out at such a speed that the vessel becomes filled with a foam of hydro-

[1] Ellis, U.S. patent, 1059720.
[2] Calvert, English patent, 18350/13.
[3] Maxted and Ridsdale, English patent, 109993/1917.

gen and oil. The plant used is illustrated in Fig. 12.

The saturation of an oil with hydrogen is a strongly exothermic reaction, and is accordingly accompanied by a considerable rise of temperature, which in a typical operation in a well insulated vessel may be as much as from 160–200° C., in the course of a hardening operation lasting from two to three hours; indeed this spontaneous rise of temperature during treatment affords an extremely useful indication that saturation has begun and is taking place with a satisfactory velocity. The velocity of absorption of hydrogen necessarily falls off as the reaction proceeds, and for this reason it is advisable in installations provided with several hydrogenation vessels to begin the hardening of successive charges at different times in order to ensure a uniform consumption of hydrogen. It has already been stated that the hydrogenation reaction follows the ordinary monomolecular formula.

The time required for the hardening operation is determined by the nature and purity of the oil, by the temperature and presssure, and by the amount of catalyst employed.

The following particulars relate to a typical hardening operation with an experimental unit of the type illustrated in Fig. 12.

The charge consisted of three-quarters of a ton of crude rape oil which was pumped from the storage tanks into the hardening vessel and heated to 140° C. by means of high pressure superheated steam passed through the heating jacket surrounding the vessel.

As soon as this requisite initial temperature had been obtained the usual proportion of nickel catalyst was added, this catalyst having been prepared by the dry reduction of nickel oxide at 350° C., and subsequent mixing, for convenience

in handling, with a small quantity of the oil for the treatment of which it was to be used.

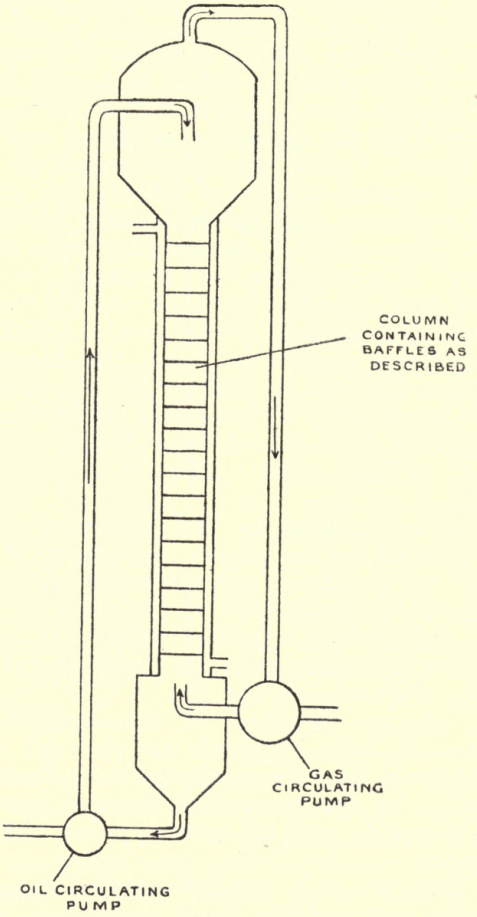


FIG. 12.

Pure hydrogen prepared from water gas by a modified intermittent process as already described

and at a pressure of 60 lb. to the square inch was now introduced into the vessel, this having been previously evacuated to eliminate air. The circulating pumps were put into action and the reaction allowed to proceed, fresh hydrogen to replace that absorbed by the oil and to maintain the pressure at 60 lb. being continuously admitted by means of an automatically constructed valve.

In two hours 1,800 cubic feet of hydrogen had been absorbed, corresponding with a reduction of iodine value from 99 to 27, and samples of the oil (which were drawn off from time to time during the operation) were found to solidify to a hard, brittle fat. The temperature of the charge had, by reason of its heat of reaction, risen from 140 C. to 185° C. in the course of the two hours' run.

The hydrogenated charge was pumped into a filtering tank and filtered while still hot by means of a steam heated filter-press of the usual type, the filtered fat being run into barrels and allowed to solidify.

The heating of the charge of oil to the requisite initial temperature for hardening without overheating and without the formation of decomposition products presents certain difficulties in practice where large volumes of oil have to be treated. It is effected in some systems by means of flue gases, while in others superheated steam is used, the latter method being preferable.

This steam is preferably employed at a pressure above the vapour pressure of water at the minimum temperature required for starting hydrogenation, so that a certain amount of condensation takes place in the heating jacket, the water resulting from this being removed by suitable traps. By adopting this procedure the large amount of latent heat evolved during the condensation of the steam is effectively utilised for heating the oil to reaction temperature and the time required for the preliminary heating

becomes very much shorter than is the case when low pressure dry superheated steam is used.

The following table contains the minimum boiler pressure required for the rapid heating of the charge in this way to various initial temperatures. In practice this pressure must be very considerably above the minimum value indicated.

Initial temperature, °C.	Minimum boiler pressure, lb. per square in.
130	25
140	39
150	56
160	76
170	101

The degree of hardness of the oil after treatment may be estimated roughly by allowing a few drops to solidify on a cold surface or more exactly by determining the "titer," *i.e.*, the melting point, under standard conditions, of the fatty acids liberated from the hardened oil by saponification. A more satisfactory determination of the degree of unsaturation is, however, obtained by measuring the iodine value or, as a quick approximation, the refractive index, these tests being the methods of control most commonly employed in practice.

The iodine value of an unsaturated oil or fatty acid may be defined as the number of grams of iodine which are taken up under standard conditions of working by 100 grams of the oil or acid in question. Saturation by iodine takes place much in the same way as by hydrogen. Thus oleic acid on being brought together with iodine under suitable conditions undergoes conversion into the saturated di-iodo-derivative according to the equation :

$$CH_3{\cdot}(CH_2)_7{\cdot}CH{:}CH{\cdot}(CH_2)_7{\cdot}COOH + I_2 = CH_3(CH_2)_7{\cdot}CHI{\cdot}CHI{\cdot}(CH_2)_7{\cdot}COOH.$$

Two methods of determination, namely, those of Hubl and Wijs, are in common use. For estima-

tions carried out according to Hubl's method, an iodine solution[1] made by dissolving 25 grams of iodine in 500 c.c. of pure 95 per cent. alcohol is employed in conjunction with a mercuric chloride solution consisting of 30 grams of $HgCl_2$ in 500 c.c. of alcohol, equal volumes of these stock solutions being mixed not more than twenty-four hours before use. In order to carry out a determination, from 0·2 to 1·0 gram of the fat, depending on the degree of saturation, is accurately weighed out and placed in a stoppered bottle of about 800 c.c. capacity. About 20 c.c. of chloroform are added to dissolve the fat, followed by 25–30 c.c. of the mixed iodine and mercuric chloride solution. The well-stoppered bottle is now placed in a dark place and allowed to stand for six to twelve hours in order to complete the reaction. The excess of iodine remaining uncombined is determined, after adding 20 c.c. of a 10 per cent. potassium iodide solution and 400 c.c. of water, by titration with a standard thiosulphate solution. During the titration, the bottle is well shaken from time to time, and as soon as the contents have become a pale yellow, starch is added as an indicator, the end-point being marked by the vanishing of the dark colour due to iodide of starch.

According to Wijs's method the iodine and mercuric chloride solutions are replaced by a solution of iodine and iodine trichloride in glacial acetic acid.

7·9 Grams of iodine trichloride and 8·7 grams of iodine[2] are dissolved separately in glacial acetic acid on a water-bath, access of moisture being avoided. The two solutions are poured into a 1-litre flask and made up to the mark with glacial acetic acid. The determination is carried out much the same as by Hubl's method, but has the important

[1] Lewkowitsch, "Technology of Oils, Fats, and Waxes," p 311 *et seq.*

[2] Lewkowitsch, *loc. cit.*

advantage that the protracted standing is unnecessary in that the reaction is usually complete in from two to three hours.

The degree of saturation of an oil may also be determined by measuring its index of refraction, this method being particularly valuable for following the course of the hardening reaction while this is proceeding and forming in this way a check on the hydrogen absorption read off from the meters attached to the plant. C. Ellis[1] gives the following typical figures for cotton oil, hydrogenated for ten hours, samples being withdrawn at the end of every hour.

Time of hydrogenation in hours.	Melting point, ° C.	Index of refraction at 55° C.
0	—	1·4588
1	28·2	1·4577
2	31·3	1·4568
3	34·3	1·4557
4	37·9	1·4549
5	40·8	1·4540
6	43·8	1·4527
7	45·6	1·4518
8	47·3	1·4510
10	55·9	1·4496

The principal uses of hardened oils are in the manufacture of soaps, of candles, of edible fats such as artificial lard, also of margarine, chocolate, etc. For edible purposes, complete elimination of nickel by filtration is essential. Bower[2] states that neutral oils do not take up even traces of nickel in a form not capable of being removed by filtering, such solution of nickel only taking place in cases where the oil contains considerable quantities of free fatty acids.

Small quantities of nickel contained in hardened fats are easily detected colorimetrically by dimethylglyoxime (Tchugaeff's reagent) the method giving

[1] C. Ellis, " Hydrogenation of Oils," p. 124.
[2] Bower, *Zeitsch. Nähr. und Genussm.*, 1912, 104.

also an approximate idea of the quantity of nickel present. The method of carrying out the reaction has been improved and standardised by Fortini [1] and by Kerr,[2] the determination being made by ashing 10–20 grams of the hardened fat, dissolving in hydrochloric acid, evaporating the solution to dryness, and igniting the residue to free it from traces of organic matter and excess of HCl. This residue is transferred to a tall 50 c.c. cylinder and moistened with a few c.c. of distilled water, 50 c.c. of standard dimethylglyoxime solution being added. A red coloration (or precipitate, if the nickel content is high) results either at once or on standing, the tint being compared with that produced under the same conditions with a nickel solution of known strength. The standard solution of dimethylglyoxime is made up by dissolving 5 grams of this body in 50 c.c. of absolute alcohol and making up to 100 c.c. with strong aqueous ammonia, the solution being kept in a well-stoppered bottle. For edible purposes, the fat should not contain more than 0·05 milligram of nickel per kilo.

[1] Fortini, *Chem. Zeit.*, 1912, **36**, 1461.
[2] Kerr, *J. Ind. and Eng. Chem.*, 1914, 207.

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